REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 074-0188

1. Agency Use Only (Leave blank)	2. Report Date	3. Report Type and Period Covered (i.e., annual 1 Jun 00 - 31 May 01)
	10 October 2006	Final Report, 07 Feb 2005 to 06 Aug 2006

4. Title and Subtitle
Evaluation of catalyst Activity - Detoxification of Chemical Warfare Agents Under Oxidation and Hydrolysis Conditions

5. Award Number
W911NF-05-C-0041

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8. Performing Organization Report Number (Leave Blank)

9. Sponsoring/Monitoring Agency Name and Address
U.S. Army RDECOM ACQ Ctr. - W911NF
4300 South Miami Blvd.
Durham, NC 22703

10. Sponsoring/Monitoring Agency Report Number (Leave Blank)
47201.1-CH-CDP

11. Supplementary Notes (i.e., report contains color photos, report contains appendix in non-print form, etc.)

12a. Distribution/Availability Statement (check one)
X Approved for public release; distribution unlimited

12b. Distribution Code
(Leave Blank)

13. Abstract ***(Maximum 200 Words)*** *(abstract should contain no proprietary or confidential information*

This project screened potential catalysts for the detoxification of chemical warfare (CW) agents by catalytic oxidation and hydrolysis under ambient conditions. TDA contacted interested researchers, who submitted their candidate catalysts directly to CUBRC (Ashford Test Site, Springville, NY). CUBRC evaluated the activity of catalysts and their ability to detoxify the chemical warfare agents GD, VX and HD. The specific focus of this test program was to screen a wide range of candidate catalyst under the same conditions using live agents. Hydrolysis catalysts were evaluated using GD and VX in buffered aqueous solution (pH 7.2). Oxidation catalysts were evaluated using VX and HD in methyl-tert-butyl ether (MTBE) solution with a headspace of air. All samples were shaken continuously on a mechanical shaker. Aliquots were removed at time intervals of t = 0, 1, 2, 6, and 22 hours and analyzed by Electron Impact - Gas Chromatography Mass Spectrometry (EI-GCMS) with high-resolution capillary chromatography. None of the catalysts evaluated displayed significant activity under the test conditions. However, some of these materials may display useful activity under other conditions.

14. Subject Terms (keywords previously assigned to proposal abstract or terms which apply to this award)
Catalyst, Decontamination, Chemical warfare, CW, BW

15. Number of Pages (count all pages including appendices) 41

16. Price Code (Leave Blank)

17. Security Classification of Report	18. Security Classification of this Page	19. Security Classification of Abstract	20. Limitation of Abstract
Unclassified	Unclassified	Unclassified	Unlimited

Evaluation of Catalyst Activity – Detoxification of Chemical Warfare Agents under Oxidation and Hydrolysis Conditions

Final Technical Report
August 15, 2006

CUBRC Contract No.: 6774
Prime Contract No.: W911-NF-05-C-0041
Subcontract No.:CBR05.1

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Contents

1. SUMMARY

Potential catalysts for the destruction and detoxification of CWA's have been submitted by individual researchers directly to CUBRC (Ashford Test Site, Springville, NY). This work was supported by a contract to TDA Research, Inc. from the U. S. Defense Threat Reduction Agency (DTRA), and subcontracted from TDA Research, Inc. to CUBRC. Catalyst samples were evaluated by CUBRC using standard testing protocols developed for evaluating the activity of catalysts and their ability to detoxify the chemical warfare agents GD (pinacolyl methylphosphonofluoridate), VX (S-[2-[bis(1-methylethyl)amino]ethyl]-O-ethyl methylphosphonothiolate) and HD [bischloroethylsulfide] under ambient conditions. Test protocol development also included developing a sample submission form to be used by submitters (Appendix 1). Completed sample submission forms as received from researchers are contained in Appendix 2.

Catalysts challenged to detoxify CWA's in aqueous conditions (hydrolysis) were evaluated using both GD and VX in buffered aqueous solution (HEPES, pH=7.2). Those challenged to detoxify CWA's in the presence of oxygen (oxidative) were evaluated using both VX and HD in methyl-tert-butyl ether (MTBE) contained in a glass vial with a headspace of air [1:3 sample volume:headspace volume]. In both tests (hydrolysis and oxidative), the samples were shaken on a mechanical shaker throughout the testing period. Aliquots of the catalyst test solutions were removed at time intervals of T= 0, 1, 2, 6, and 22 hours and analyzed for each agent by Electron Impact – Gas Chromatography Mass Spectrometry (EI-GCMS) with high resolution capillary chromatography. Chromatographic peaks were also examined to identify potential degradation products which may also be hazardous. Unknown chromatographic peaks were tentatively identified based upon matching the mass spectrum obtained with the NIST Mass Spectral Library Database - NIST/EPA/NIH. Blank control and spiked reference samples were also prepared in duplicate with each test as a comparison.

2. EXPERIMENTAL

2.1 Standard test protocol for hydrolysis of agents GD and VX:

1. In duplicate, add 2.4 mg of catalyst to 10 ml of buffered aqueous solution (50 mM HEPES, pH = 7.2) contained in a 40 ml glass amber VOA vial. Test and record (pre-test) the pH of buffer/catalyst solution.
2. In duplicate, prepare 40 ml glass amber vials containing 10 ml of buffered aqueous solution (HEPES, pH = 7.2) to be run as control samples with each batch of samples.
3. Add 12 ul of neat agent (VX or GD) to each vial, cap and votex for 30 sec. Transfer to a mechanical shaker.
4. Add 4 ul of neat agent (VX or GD) into a glass vial containing 10 ml chloroform as a reference solution.
5. At time periods of T=0, 1, 2, 6, and 22 hrs, remove a 1 ml aliquot from each sample and transfer to a 7 ml glass vial containing 3.0 ml $CHCl_3$. Vortex for 1 min and transfer an aliquot of the organic phase to an auto-sampler vial for GCMS analysis. Test and record (post-test) the pH of the catalyst mixture after the last sample is extracted (22 hrs).

2.2 Standard test protocol for oxidation of agents HD and VX:

6. In duplicate, add 0.8 mg of catalyst to 10 ml of MTBE contained in a 40 ml glass amber VOA vial.
7. In duplicate, prepare 40 ml glass amber vials containing 10 ml of MTBE to be run as reference/control samples with each batch of samples.
8. Add 4 ul of neat agent (VX or HD) to each vial, cap and vortex for 30 sec. Transfer to a mechanical shaker.
9. At time periods of T=0, 1, 2, 6, and 22 hrs, remove an aliquot from each sample and transfer to 200 ul micro insert contained in an auto-sampler vial (with no headspace) for GCMS analysis.

2.3 Modifications to Test Protocol – TAML Catalyst (Carnegie Mellon University)

A minimal amount (3.3 mg) of TAML catalyst was received from Carnegie Mellon University (CMU). This amount was insufficient to carry out both the hydrolysis and oxidative tests in duplicate according to the standard test protocols above. A suggested protocol was documented in the correspondence received with the sample submission form from CMU. It stated that TAML is a high efficiency catalyst and that therefore it is required in much smaller amounts (catalyst:substrate ~1:100 or more). The correspondence also recommended making up the catalyst in a concentration of 0.1 mg/ml DI water, and using 0.2 mg TAML catalyst/4 mg neat agent. Based upon this information the 3.3 mg of TAML catalyst received was dissolved in 30 ml of DI water (0.107 mg/ml). For the hydrolysis tests, 6 ml of this solution (0.6 mg) was added to 4 ml HEPES buffer solution and 12 ul neat agent (VX or GD). Control samples consisted of 6 ml DI water and 4 ml HEPES buffer solution with 12 ul neat agent (VX or GD). For the oxidative tests, 1 ml of this solution (0.1 mg) was added to 4 or 5 ml MTBE and 2 ul neat agent (HD or VX respectively). Control samples consisted of 1 ml DI water and 4 or 5 ml MTBE with 2 ul neat agent (HD or VX respectively).

3. GAS CHROMATOGRPAHY/MASS SPECTROMETRY (GC/MS) CONDITIONS

Instrument:	Agilent Model 5973 Network Mass Spectrometer equipped with electron impact (EI) ion source, 6890N Gas Chromatograph and Model 7683B Automatic Sampler
Column:	30 m x 0.25 mm i.d. DB-5MS (Cross-linked methyl silicone), fused silica capillary column, 0.25 um film thickness (J & W Scientific Cat. No. 122-5536)
Carrier Gas Flow Rate:	1.2 ml/min Helium Constant Flow
Column Temperature:	40^{o}C initial temp., hold 1 min., 8^{o}C/min to 250^{o}C, hold 5 min.
Injection Temperature:	250^{o}C
Injection Volume/Type:	1 µL splitless injection (4 mm i.d. glass Goose neck liner) with 1.5 min. purge activation time. Split vent flow rate @ 75 ml /min.
MS Source Temperature:	230^{o}C
EM Voltage:	1100V
Solvent Delay:	6 min.
Data Collection:	50 to 550 amu at a scan rate of 2.0 scans/sec, threshold of 50 and sampling of 2.
Data System:	Agilent Enhanced MSD ChemStation (Version D.02.00.275)

3.1 GC-MS Data Analysis and Identification of Degradation Products

The GCMS data was acquired and processed using Agilent ChemStation software. Chemical agents (VX, GD, HD) were identified by comparison of the retention time and mass spectra of calibration standards. The concentration of the agents was calculated by external standardization using reference standards which were analyzed with each set of data. Calibration standards of VX and HD at concentrations of 5.0, 12, 24, 46, 83, 250 and 500 ng/ul were prepared in MTBE for the oxidative tests. Calibration standards of VX and GD at concentrations of 5.0, 12, 24, 46, 83, 250 and 500 ng/ul were prepared in $CHCl_3$, for the hydrolysis tests. Calibration curves were generated in Excel using a second order polynomial fit. Non- agent chromatographic peaks greater than 10% of T=0 concentration were examined to identify potential degradation products based upon matching the mass spectrum obtained with the NIST Mass Spectral Library Database - NIST/EPA/NIH Version 2.0 (2002). The amount (ug/sample) of degradation products were estimated based upon using an average response factor calculated from the respective reference standards.

The following are representative chromatograms and calibration curves of VX, GD and HD:

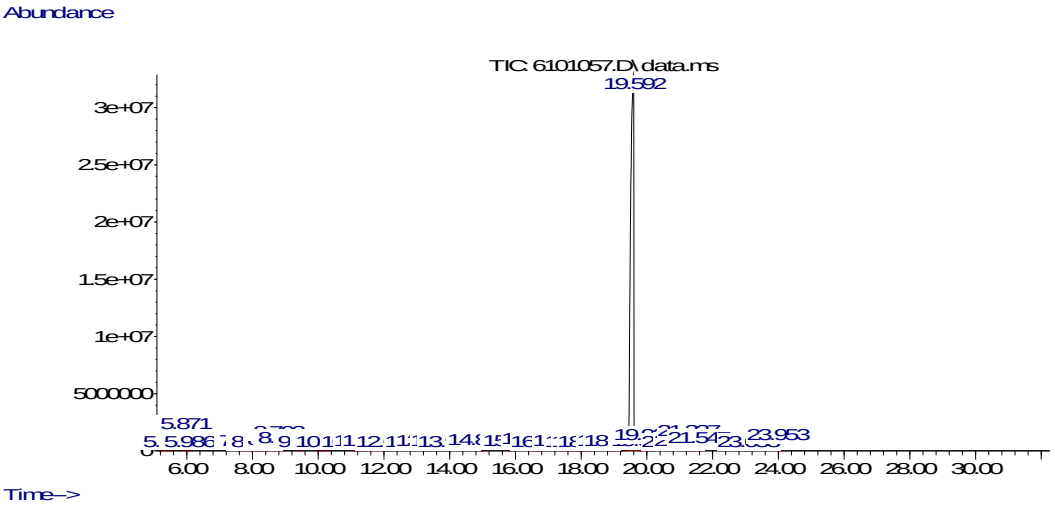


Figure 1: Chromatogram representing injection of 500 ng of VX in CHCl3

Figure 2: VX Calibration Curve (23.8 – 500 ng)

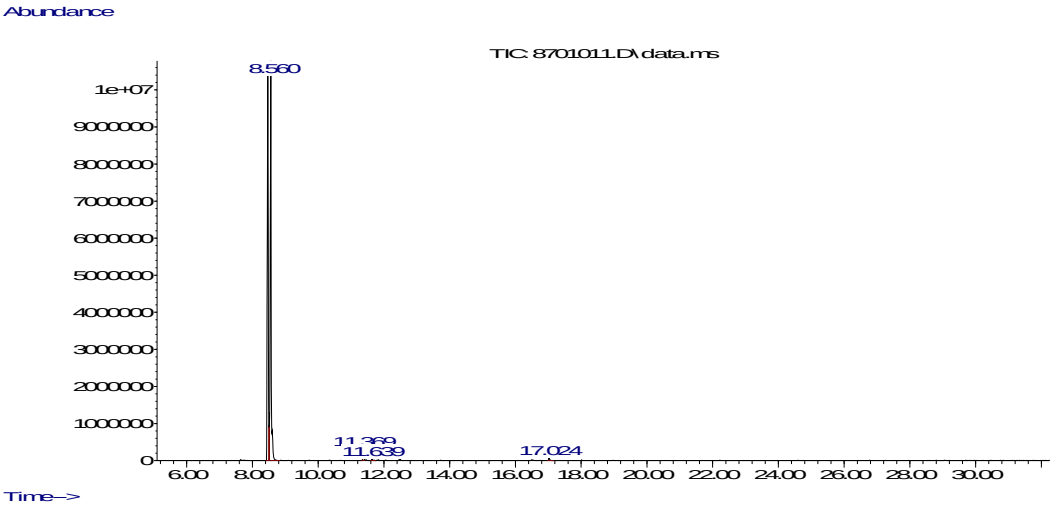


Figure 3: **Chromatogram representing injection of 500 ng of GD in CHCl3**

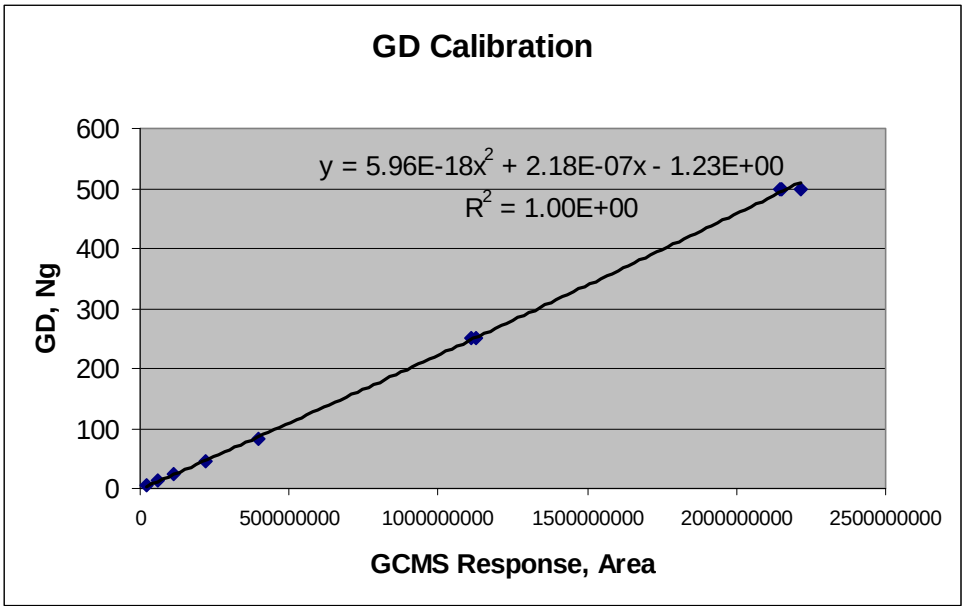


Figure 4: **GD Calibration Curve (23.8 – 500 ng)**

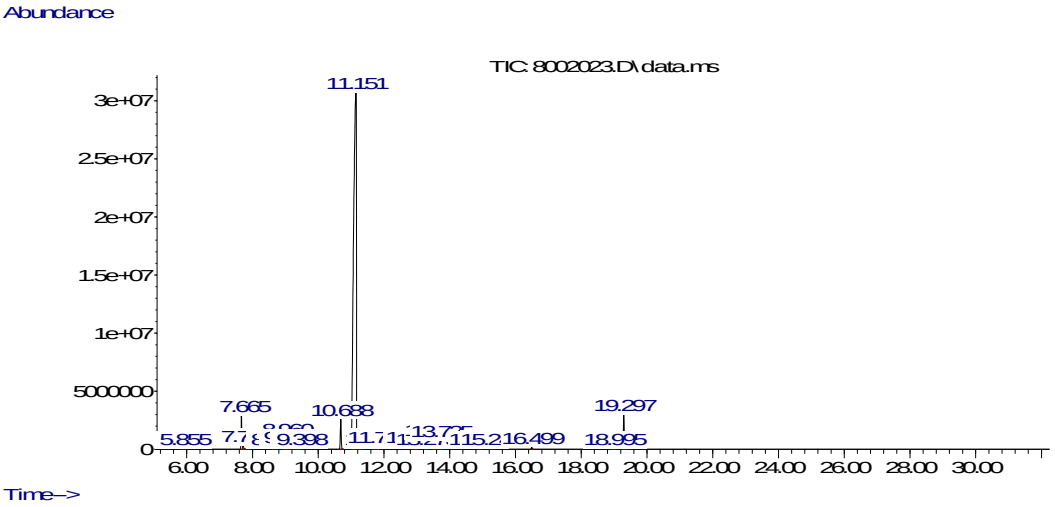


Figure 5: Chromatogram representing injection of 500 ng of HD in MTBE

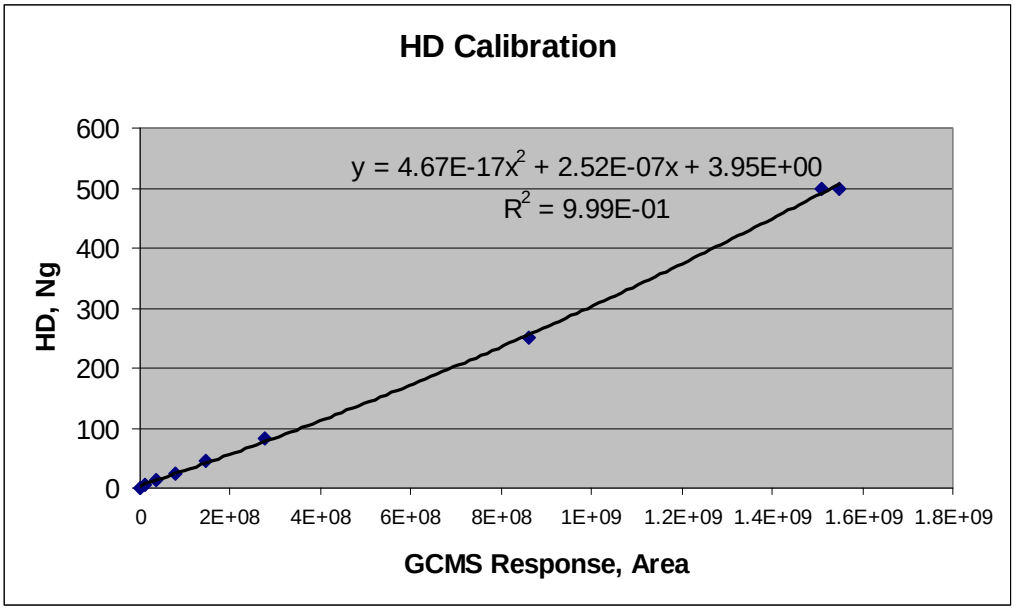


Figure 6: HD Calibration Curve (23.8 – 500 ng)

4. EXPERIMENTAL TEST DESIGN

Testing of catalyst samples was determined based upon the time samples were received, priorities indicated by the submitter (if multiple catalyst were submitted), and priorities established by TDA. The following Tables 1.A and 1.B indicate which catalysts where analyzed on each Test date, the type of test (hydrolysis or oxidative), define how the catalysts were identified within the laboratory, and give a brief description of each catalyst as received from the submitter.

4.1 Naming convention for Catalyst Evaluation samples

Example Sample ID: 3 Hy VX-1

3: Sample number taken from TDA priority list, or QC type, BLK is spiked buffer, Ref is spiked solvent

Hy: Test type, hydrolysis (Hy) or oxidation (Ox)

VX: Agent (VX, GD, HD)

1: Replicate number 1 or 2 (all samples were analyzed in duplicate)

Table 1.A Experimental Test Design - Hydrolysis Testing

Test No.	Date	Type Test	Sample Description	Lab ID's	Researcher	Researcher Submittal Date	Sample No.	Catalyst Type
Test 1	4/24/2006	VX Hydrolysis	3	3 Hy VX-1 3 Hy VX-2	Suib	9/23/2005	K-OMS-2	Transition metal oxide catalyst
			4	4 Hy VX-1 4 Hy VX-2	Spivey	10/5/2005	Biaryl organocatalyst 1	
			5	5 Hy VX-1 5 Hy VX-2	Ford	10/7/2005	RK83-BIV-091A	Anion exchange polymer latex in water, 95 mg/mL
			7	7 Hy VX-1 7 Hy VX-2	Collins	10/28/2005	TAML	TAML catalyst; metal-centered enzyme mimic
Test 2	4/27/2006	VX Hydrolysis	10	10 Hy VX-1 10 Hy VX-2	Bell	11/16/2005	TDA-5-Ni	Transition-metal-centered enzyme mimic
			12	12 Hy VX-1 12 Hy VX-2	Suib	9/23/2005	Fe-K-OMS-2	Transition metal oxide catalyst
			13	13 Hy VX-1 13 Hy VX-2	Spivey	10/5/2005	Biaryl organocatalyst 2	
			14	14 Hy VX-1 14 Hy VX-2	Ford	10/7/2005	RK83-BIV-091B	Anion exchange polymer latex, dry
Test 3	5/2/2006	GD Hydrolysis	3	3 Hy GD-1 3 Hy GD-2	Suib	9/23/2005	K-OMS-2	Transition metal oxide catalyst
			4	4 Hy GD-1 4 Hy GD-2	Spivey	10/5/2005	Biaryl organocatalyst 1	
			5	5 Hy GD-1 5 Hy GD-2	Ford	10/7/2005	RK83-BIV-091A	Anion exchange polymer latex in water, 95 mg/mL
			7	7 Hy GD-1 7 Hy GD-2	Collins	10/28/2005	TAML	TAML catalyst; metal-centered enzyme mimic
Test 4	5/4/2006	GD Hydrolysis	10	10 Hy GD-1 10 Hy GD-2	Bell	11/16/2005	TDA-5-Ni	Transition-metal-centered enzyme mimic
			12	12 Hy GD-1 12 Hy GD-2	Suib	9/23/2005	Fe-K-OMS-2	Transition metal oxide catalyst
			13	13 Hy GD-1 13 Hy GD-2	Spivey	10/5/2005	Biaryl organocatalyst 2	
			14	14 Hy GD-1 14 Hy GD-2	Ford	10/7/2005	RK83-BIV-091B	Anion exchange polymer latex, dry

Table 1.B Experimental Test Design - Oxidation Testing

Test No.	Date	Type Test	Sample Description	Lab ID's	Researcher	Researcher Submittal Date	Sample No.	Catalyst Type
Test 5	5/9/2006	HD Oxidation	1	1 Ox HD-1 1 Ox HD-2	Landry	9/16/2005	SL	Metal oxide supported on SiO2
			2	2 Ox HD-1 2 Ox HD-2	Wu	9/23/2005	Pt/BN	1.1% Pt supported on boron nitride
			3	3 Ox HD-1 3 Ox HD-2	Suib	9/23/2005	K-OMS-2	Transition metal oxide catalyst
			6	6 Ox HD-1 6 Ox HD-2	Wenjie	10/18/2005	Black Powder	Noble metal supported on mixed oxides
Test 6	5/11/2006	HD Oxidation	7	7 Ox HD-1 7 Ox HD-2	Collins	10/28/2005	TAML	TAML catalyst; metal-centered enzyme mimic
			8	8 Ox HD-1 8 Ox HD-2	Pinnavaia	11/1/2005	Sample 1	Cobalt complex supported on metal oxide
			9	9 Ox HD-1 9 Ox HD-2	Hill/Luo	11/18/2005	ZL-004	POM
			11	11 Ox HD-1 11 Ox HD-2	Landry	9/16/2005	DK	POM supported on SiO2
Test 7	5/17/2006	VX Oxidation	1	1 Ox VX-1 1 Ox VX-2	Landry	9/16/2005	SL	Metal oxide supported on SiO2
			2	2 Ox VX-1 2 Ox VX-2	Wu	9/23/2005	Pt/BN	1.1% Pt supported on boron nitride
			3	3 Ox VX-1 3 Ox VX-2	Suib	9/23/2005	K-OMS-2	Transition metal oxide catalyst
			6	6 Ox VX-1 6 Ox VX-2	Wenjie	10/18/2005	Black Powder	Noble metal supported on mixed oxides
Test 8	5/18/2006	VX Oxidation	7	7 Ox VX-1 7 Ox VX-2	Collins	10/28/2005	TAML	TAML catalyst; metal-centered enzyme mimic
			8	8 Ox VX-1 8 Ox VX-2	Pinnavaia	11/1/2005	Sample 1	Cobalt complex supported on metal oxide
			9	9 Ox VX-1 9 Ox VX-2	Hill/Luo	11/18/2005	ZL-004	POM
			11	12 Ox VX-1 12 Ox VX-2	Suib	9/23/2006	Fe-K-OMS-2	transition metal oxide catalyst

5. RESULTS

Tables 2-3 and Figures 7-8 show a summary of the amount of VX (mg) determined for catalyst samples 3, 4, 5, 7 [Test 1 - Hydrolysis] and samples 10, 12, 13 and 14 [Test 2 - Hydrolysis] at each time period (T=0, 1, 2, 6, and 22 hrs.) and the theoretical % remaining for each time period based upon the amount of VX added to each sample (15.125 mg). Tables 2-3 also show the pH of the buffered catalyst solutions pre and post-test. After 22 hours, there appeared to be no difference between the amount of VX determined in the blank control samples (without catalyst) and the catalyst samples in a HEPES, pH 7.2 buffer solution at ambient temperature.

Tables 4-5 and Figures 9-10 show a summary of the amount of GD (mg) determined for catalyst samples 3, 4, 5, 7 [Test 3 - Hydrolysis] and samples 10, 12, 13 and 14 [Test 4 - Hydrolysis] at each time period (T=0, 1, 2, 6, and 22 hrs) and the theoretical % remaining for each time period based upon the amount of GD added to each sample (12.1 mg). Tables 4-5 also show the pH of the buffered catalyst solutions pre and post-test. After 22 hours, there was an approximately 60% decrease in the amount of GD determined in catalyst samples 3, 4, 5, 12, 13, and 14 and the corresponding blank control samples (10 ml HEPES buffer solution without catalyst). There was a 70 % decrease in the amount of GD for catalyst 10. Catalyst 7 and the corresponding blank control samples were prepared differently (see above "Modifications to Test Protocol – TAML Catalyst (Carnegie Mellon University)" and both showed a 30% decrease in GD amount after 22 hours. Table 15 contains a list of possible GD degradation products as identified in the GCMS chromatogram based upon comparison of obtained mass spectra to NIST mass spectral library data base. Figure 15 shows a representative chromatogram of catalyst sample 5 at time 22 hrs. Tables 16-17 contain the amount of degradation products (ug) determined for Test 3 and 4.

The amount of the degradation products(ug/sample) were estimated based upon using an average response factor calculated from the GD calibration standards. Note that the EI spectra for the majority of GD degradation compounds do not exhibit strong MW ions; therefore positive identification is difficult without reference standards or analysis by CI GC/MS. It is important to note that the degradation products which are non-extractable or non-chromatographable (e.g. acids) may be present in the buffered catalyst solution but are not identifiable. Also it is difficult to asess the effectiveness of a catalyst based upon the amounts of a particular degradation product, since it may be an intermediate or secondary byproduct which may either increase or decrease over time at various rates.

Appendix 3 contains representative mass spectra for each of the potential GD degradation products obtained at the respective GCMS retention times.

Tables 6-7 and Figures 11-12 show a summary of the amount of HD (mg) determined for catalyst samples 1, 2, 3, 6 [Test 5 - Oxidative] and samples 7, 8, 9 and 11 [Test 6 - Oxidative] at each time period (T=0, 1, 2, 6, and 22 hrs) and the theoretical % remaining for each time period based upon the amount of HD added to each sample (5.08 mg). After 22 hours, there appeared to be no difference between the amount of HD determined in the blank reference control samples (without catalyst) and the catalyst samples in MTBE (with air headspace) at ambient temperature.

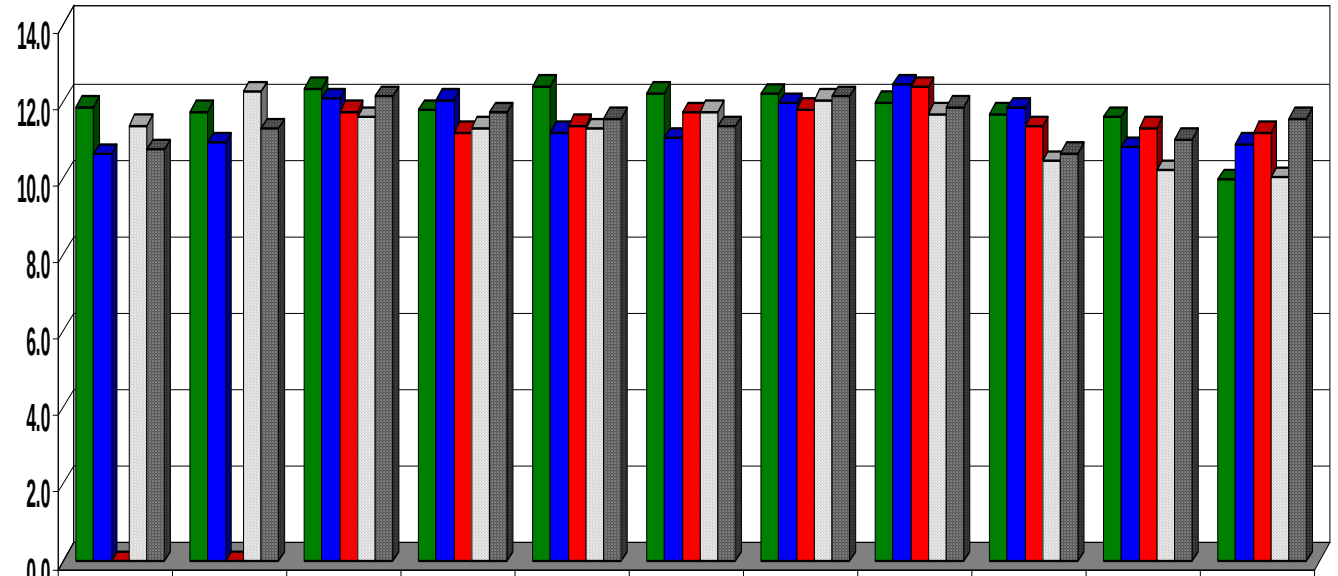
Tables 8-9 and Figures 13-14 show a summary of the amount of VX (mg) determined for catalyst samples 1, 2, 3, 6 [Test 7 - Oxidative] and samples 7, 8, 9, and 11 [Test 8 - Oxidative] at each time period (T=0, 1, 2, 6, and 22 hrs) and the theoretical % remaining for each time period based upon the amount of VX added to each sample (4.08 mg). After 22 hours, there appeared to be no difference between the amount of VX determined in the blank reference control samples (without catalyst) and the catalyst samples in MTBE (with air headspace) at ambient temperature.

Table 2. VX in Catalyst Test Solutions under Hydrolysis Condition (HEPES, pH 7.2) at Time 0, 1, 2, 6 and 22 Hr. – Test 1

	VX, mg										pH	
Sample Description	0 Hr	%, Theo.[1/]	1 Hr	%, Theo.[1/]	2 Hr	%, Theo.[1/]	6 Hr	%, Theo.[1/]	22 Hr	%, Theo.[1/]	Pre-Test	Post-Test
Blk1 Hy VX-1 [2/]	11.9	98	10.6	88	Sple lost[3/]		11.4	94	10.7	89	7.3	7.3
Blk1 Hy VX-2 [2/]	11.7	97	10.9	90	Sple lost[3]		12.2	101	11.3	93	7.3	7.3
Blk1 Hy VX-3 [2/]	12.3	102	12.1	100	11.7	97	11.6	96	12.1	100	NA	NA
3 Hy VX-1	11.8	97	12.0	100	11.2	92	11.3	94	11.7	97	7.2	7.3
3 Hy VX-2	12.4	103	11.2	92	11.4	94	11.3	93	11.6	95	7.2	7.3
4 Hy VX-1	12.2	101	11.0	91	11.7	97	11.7	97	11.4	94	7.3	7.4
4 Hy VX-2	12.2	101	12.0	99	11.8	97	12.1	100	12.1	100	7.3	7.4
5 Hy VX-1	12.0	99	12.4	103	12.4	102	11.7	97	11.9	98	7.2	7.4
5 Hy VX-2	11.7	97	11.8	98	11.3	94	10.4	86	10.6	88	7.2	7.4
7 Hy VX-1	11.6	96	10.8	89	11.3	94	10.2	84	11.0	91	7.3	7.6
7 Hy VX-2	10.0	82	10.9	90	11.2	92	10.0	83	11.6	96	7.3	7.6

1/ % Theo. = % Theoretical amount of VX added to HEPES buffer solution (12.1 mg)
2/ Blk 1 Hy VX-1, Blk Hy VX-2 and Blk Hy VX-3 were Control samples prepared from 10 ml HEPES Buffer solution and 12 ul VX.
3/ Sample Lost

Figure 7: Graphical Representation of VX in Test Solutions under Hydrolysis Condition (HEPES, pH 7.2) at Time 0, 1, 2, 6 and 22 Hr. – Test 1



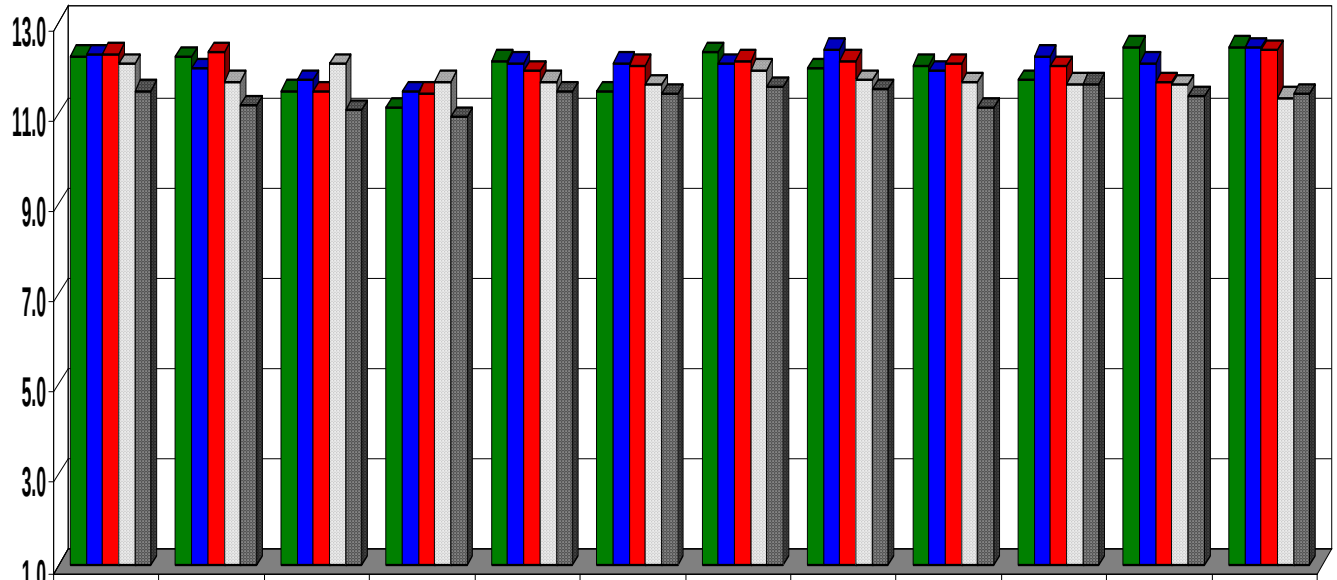
	Blk1 Hy VX-1	Blk1 Hy VX-2	Blk1 Hy VX-3	3 Hy VX-1	3 Hy VX-2	4 Hy VX-1	4 Hy VX-2	5 Hy VX-1	5 Hy VX-2	7 Hy VX-1	7 Hy VX-2
0 Hr	11.9	11.7	12.3	11.8	12.4	12.2	12.2	12.0	11.7	11.6	10.0
1 Hr	10.6	10.9	12.1	12.0	11.2	11.0	12.0	12.4	11.8	10.8	10.9
2 Hr	0.0	0.0	11.7	11.2	11.4	11.7	11.8	12.4	11.3	11.3	11.2
6 Hr	11.4	12.2	11.6	11.3	11.3	11.7	12.1	11.7	10.4	10.2	10.0
22 Hr	10.7	11.3	12.1	11.7	11.6	11.4	12.1	11.9	10.6	11.0	11.6

Table 3. VX in Catalyst Test Solutions under Hydrolysis Condition (HEPES, pH 7.2) at Time 0, 1, 2, 6 and 22 Hr. – Test 2

	VX, mg										pH	
Sample Description	0 Hr	%, Theo.[1/]	1 Hr	%, Theo.[1/]	2 Hr	%, Theo.[1/]	6 Hr	%, Theo.[1/]	22 Hr	%, Theo.[1/]	Pre-Test	Post-Test
Blk2 Hy VX-1 [2/]	12.3	102	12.3	102	12.4	102	12.1	100	11.5	95	7.2	7.5
Blk2 Hy VX-2 [2/]	12.3	102	12.0	99	12.4	102	11.7	97	11.2	92	7.2	7.4
Blk2 Hy VX-3 A [3/]	11.5	95	11.8	97	11.5	95	12.1	100	11.1	92	7.2	7.3
Blk2 Hy VX-3 B [3/]	11.1	92	11.5	95	11.5	95	11.7	97	10.9	90	7.3	7.4
10 Hy VX-1	12.2	101	12.1	100	12.0	99	11.7	97	11.5	95	7.2	7.3
10 Hy VX-2	11.5	95	12.1	100	12.1	100	11.7	96	11.5	95	7.2	7.3
12 Hy VX-1	12.4	102	12.1	100	12.2	101	12.0	99	11.6	96	7.3	7.4
12 Hy VX-2	12.0	99	12.5	103	12.2	101	11.8	97	11.6	96	7.3	7.4
13 Hy VX-1	12.1	100	12.0	99	12.1	100	11.7	97	11.2	92	7.3	7.4
13 Hy VX-2	11.8	97	12.3	102	12.1	100	11.7	97	11.7	97	7.3	7.4
14 Hy VX-1	12.5	103	12.2	100	11.7	97	11.7	96	11.4	94	7.3	7.4
14 Hy VX-2	12.5	103	12.5	103	12.4	103	11.4	94	11.4	95	7.3	7.4

1/ % Theo. = % Theoretical amount of VX added to HEPES buffer solution (12.1 mg)
2/ Blk 2 Hy VX-1 and Blk 2 Hy VX-2 were Control samples prepared from 10 ml HEPES Buffer solution and 12 ul VX.
3/ Blk 2 Hy VX-3 A and Blk 2 Hy VX-3 B were Control samples prepared from 6 ml DI water, 4 ml HEPES buffer solution and 12 ul VX.

Figure 8: **Graphical Representation of VX in Test Solutions under Hydrolysis Condition (HEPES, pH 7.2) at Time 0, 1, 2, 6 and 22 Hr. – Test 2**



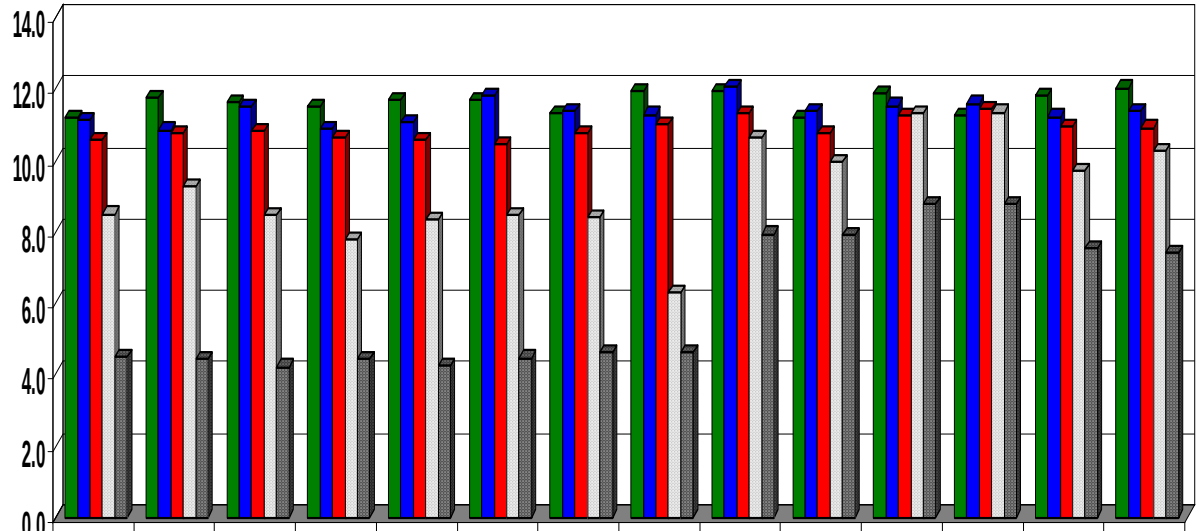
	Blk2 Hy VX-1	Blk2 Hy VX-2	Blk2 Hy VX-3 A	Blk2 Hy VX-3 B	10 Hy VX-1	10 Hy VX-2	12 Hy VX-1	12 Hy VX-2	13 Hy VX-1	13 Hy VX-2	14 Hy VX-1	14 Hy VX-2
0 Hr	12.3	12.3	11.5	11.1	12.2	11.5	12.4	12.0	12.1	11.8	12.5	12.5
1 Hr	12.3	12.0	11.8	11.5	12.1	12.1	12.1	12.5	12.0	12.3	12.2	12.5
2 Hr	12.4	12.4	11.5	11.5	12.0	12.1	12.2	12.2	12.1	12.1	11.7	12.4
6 Hr	12.1	11.7	12.1	11.7	11.7	11.7	12.0	11.8	11.7	11.7	11.7	11.4
22 Hr	11.5	11.2	11.1	10.9	11.5	11.5	11.6	11.6	11.2	11.7	11.4	11.4

Table 4. GD in Catalyst Test Solutions under Hydrolysis Condition (HEPES, pH 7.2) at Time 0, 1, 2, 6 and 22 Hr. – Test 3

	GD, mg										pH	
Sample Description	0 Hr	%, Theo.[1/]	1 Hr	%, Theo.[1/]	2 Hr	%, Theo.[1/]	6 Hr	%, Theo.[1/]	22 Hr	%, Theo.[1/]	Pre-Test	Post-Test
Blk3 Hy GD-1 [2/]	11.2	93	11.1	92	10.6	87	8.5	70	4.5	37	7.3	6.9
Blk3 Hy GD-2 [2/]	11.8	97	10.8	90	10.8	89	9.2	76	4.4	37	7.3	6.9
3 Hy GD-1	11.6	96	11.5	95	10.8	90	8.5	70	4.2	35	7.2	6.9
3 Hy GD-2	11.5	95	10.9	90	10.6	88	7.8	64	4.4	37	7.2	6.9
4 Hy GD-1	11.7	97	11.0	91	10.6	87	8.4	69	4.2	35	7.3	6.9
4 Hy GD-2	11.7	97	11.8	98	10.4	86	8.5	70	4.5	37	7.3	6.9
5 Hy GD-1	11.3	94	11.4	94	10.8	89	8.4	69	4.6	38	7.3	6.9
5 Hy GD-2	11.9	99	11.3	93	11.0	91	6.3	52	4.6	38	7.3	6.9
7 Hy GD-1	11.9	99	12.1	100	11.3	94	10.6	88	7.9	66	7.3	6.7
7 Hy GD-2	11.2	92	11.4	94	10.8	89	9.9	82	7.9	65	7.3	6.7
H2O Blk3 Hy GD-1[4/]	11.9	98	11.5	95	11.2	93	11.3	94	8.8	73	7.0	2.7
H2O Blk3 Hy GD-2[4/]	11.2	93	11.6	96	11.4	94	11.3	94	8.8	72	7.0	2.7
Blk3 Hy GD-3 [3/]	11.8	97	11.2	93	10.9	90	9.7	80	7.5	62	7.3	6.7
Blk3 Hy GD-4 [3/]	12.0	99	11.4	94	10.9	90	10.2	85	7.4	61	7.3	6.7

1/ % Theo. = % Theoretical amount of GD added to HEPES buffer solution (12.2 mg)
2/ Blk 3 Hy GD-1 and Blk 3 Hy GD-2 were Control samples prepared from 10 ml HEPES Buffer solution and 12 ul GD.
3/ Blk 3 Hy GD-3 and Blk 3 Hy GD-4 were Control samples prepared from 6 ml DI water, 4 ml HEPES buffer solution and 12 ul GD.
4/ H2O Blk 3 Hy GD-1 and H2O Blk 3 Hy GD-2 were Control samples prepared from 10 ml DI water and 12 ul GD.

Figure 9: **Graphical Representation of GD in Test Solutions under Hydrolysis Condition (HEPES, pH 7.2) at Time 0, 1, 2, 6 and 22 Hr. – Test 3**



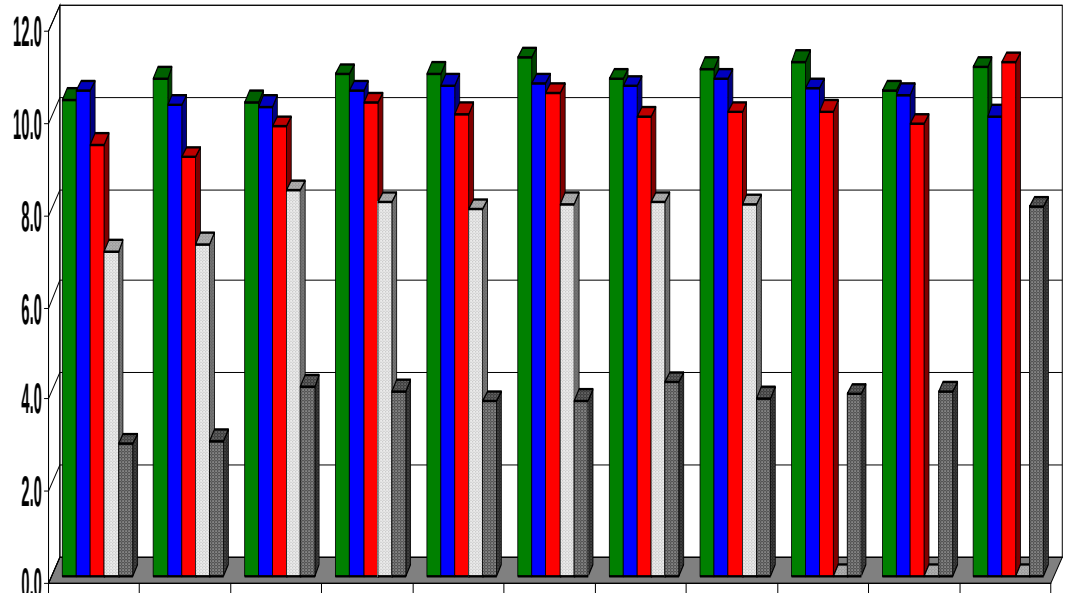
	Blk3 Hy GD-1	Blk3 Hy GD-2	3 Hy GD-1	3 Hy GD-2	4 Hy GD-1	4 Hy GD-2	5 Hy GD-1	5 Hy GD-2	7 Hy GD-1	7 Hy GD-2	H2O Blk3 Hy GD-1	H2O Blk3 Hy GD-2	Blk3 Hy GD-3	Blk3 Hy GD-4
0 Hr	11.2	11.8	11.6	11.5	11.7	11.7	11.3	11.9	11.9	11.2	11.9	11.2	11.8	12.0
1 Hr	11.1	10.8	11.5	10.9	11.0	11.8	11.4	11.3	12.1	11.4	11.5	11.6	11.2	11.4
2 Hr	10.6	10.8	10.8	10.6	10.6	10.4	10.8	11.0	11.3	10.8	11.2	11.4	10.9	10.9
6 Hr	8.5	9.2	8.5	7.8	8.4	8.5	8.4	6.3	10.6	9.9	11.3	11.3	9.7	10.2
22 Hr	4.5	4.4	4.2	4.4	4.2	4.5	4.6	4.6	7.9	7.9	8.8	8.8	7.5	7.4

Table 5. GD in Catalyst Test Solutions under Hydrolysis Condition (HEPES, pH 7.2) at Time 0, 1, 2, 6 and 22 Hr. – Test 4

	GD, mg										pH	
Sample Description	0 Hr	%, Theo.[1/]	1 Hr	%, Theo.[1/]	2 Hr	%, Theo.[1/]	6 Hr	%, Theo.[1/]	22 Hr	%, Theo.[1/]	Pre-Test	Post-Test
10 Hy GD-1	10.3	86	10.5	87	9.4	77	7.1	58	2.9	24	7.2	6.7
10 Hy GD-2	10.8	89	10.2	85	9.1	75	7.2	60	2.9	24	7.2	6.7
12 Hy GD-1	10.3	85	10.2	84	9.8	81	8.4	69	4.1	34	7.2	6.8
12 Hy GD-2	10.9	90	10.5	87	10.3	85	8.1	67	4.0	33	7.2	6.8
13 Hy GD-1	10.9	90	10.7	88	10.0	83	8.0	66	3.8	31	7.2	6.9
13 Hy GD-2	11.3	93	10.7	88	10.5	87	8.1	67	3.8	32	7.2	6.9
14 Hy GD-1	10.8	89	10.6	88	10.0	82	8.1	67	4.2	35	7.2	6.8
14 Hy GD-2	11.0	91	10.8	89	10.1	83	8.1	67	3.9	32	7.2	6.8
Blk4 Hy GD-1 [2/]	11.2	92	10.6	87	10.1	83	Sple lost[4/]	0	3.9	33	7.2	6.8
Blk4 Hy GD-2 [2/]	10.5	87	10.5	86	9.8	81	Sple lost[4/]	0	4.0	33	7.2	6.8
H2O Blk Hyd-2 [3/]	11.0	91	10.0	83	11.1	92	Sple lost[4/]	0	8.0	66	NA	2.8

1/ % Theo. = % Theoretical amount of GD added to HEPES buffer solution (12.2 mg)
2/ Blk 4 Hy GD-1 and Blk 4 Hy GD-2 were Control samples prepared from 10 ml HEPES Buffer solution and 12 ul GD.
3/ H2O Blk Hy - 2 was a Control sample prepared from 10 ml DI water and 12 ul GD.
4/ Sample Lost

Figure 10: Graphical Representation of GD in Test Solutions under Hydrolysis Condition (HEPES, pH 7.2) at Time 0, 1, 2, 6 and 22 Hr. – Test 4



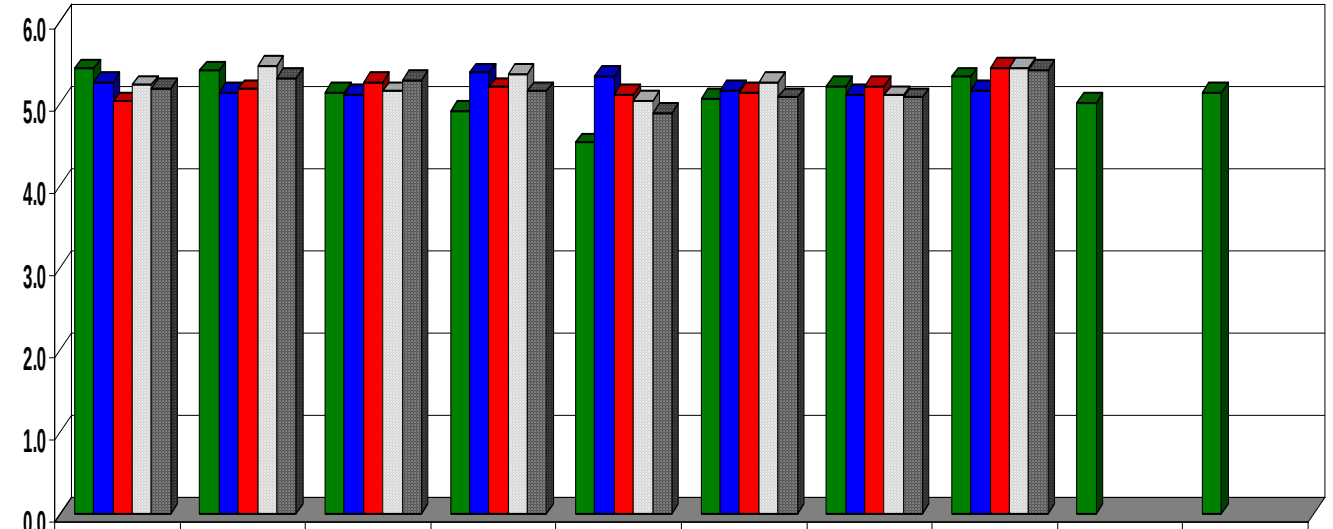
	10 Hy GD-1	10 Hy GD-2	12 Hy GD-1	12 Hy GD-2	13 Hy GD-1	13 Hy GD-2	14 Hy GD-1	14 Hy GD-2	Blk4 Hy GD-1	Blk4 Hy GD-2	H2O Hyd-2
0 Hr	10.3	10.8	10.3	10.9	10.9	11.3	10.8	11.0	11.2	10.5	11.0
1 Hr	10.5	10.2	10.2	10.5	10.7	10.7	10.6	10.8	10.6	10.5	10.0
2 Hr	9.4	9.1	9.8	10.3	10.0	10.5	10.0	10.1	10.1	9.8	11.1
6 Hr	7.1	7.2	8.4	8.1	8.0	8.1	8.1	8.1	0.0	0.0	0.0
22 Hr	2.9	2.9	4.1	4.0	3.8	3.8	4.2	3.9	3.9	4.0	8.0

Table 6. HD in Catalyst Test Solutions under Oxidative Conditions at Time 0, 1, 2, 6 and 22 Hr. – Test 5

	GD, mg									
Sample Description	0 Hr	%, Theo.[1/]	1 Hr	%, Theo.[1/]	2 Hr	%, Theo.[1/]	6 Hr	%, Theo.[1/]	22 Hr	%, Theo.[1/]
1 Ox HD-1	5.4	107	5.3	104	5.0	99	5.2	103	5.2	102
1 Ox HD-2	5.4	106	5.1	101	5.2	102	5.5	108	5.3	105
2 Ox HD-1	5.2	101	5.1	101	5.3	104	5.2	102	5.3	104
2 Ox HD-2	4.9	97	5.4	106	5.2	103	5.4	106	5.2	101
3 Ox HD-1	4.5	89	5.3	105	5.1	101	5.1	99	4.9	96
3 Ox HD-2	5.1	100	5.2	102	5.1	101	5.3	104	5.1	100
6 Ox HD-1	5.2	103	5.1	101	5.2	103	5.1	101	5.1	100
6 Ox HD-2	5.3	105	5.2	102	5.4	107	5.5	107	5.4	107
Ref 5 OX HD-1 [2/]	5.0	99								
Ref 5 OX HD-2 [2/]	5.1	101								

1/ % Theo. = % Theoretical amount of HD added to MTBE (5.08 mg)
2/ Ref 5 Ox HD-1 and Ref 5 Ox HD-2 samples were MTBE spiked with HD (5.08 mg) and used as control samples. The samples were also analyzed every 10 samples during a GCMS sequence and no degradation was observed.

Figure 11: Graphical Representation of HD in TDA Catalyst Test Solutions (Test 5)



	1 Ox HD-1	1 Ox HD-2	2 Ox HD-1	2 Ox HD-2	3 Ox HD-1	3 Ox HD-2	6 Ox HD-1	6 Ox HD-2	Ref5 Hy GD-1	Ref5 Hy GD-2
0 Hr	5.4	5.4	5.2	4.9	4.5	5.1	5.2	5.3	5.0	5.1
1 Hr	5.3	5.1	5.1	5.4	5.3	5.2	5.1	5.2		
2 Hr	5.0	5.2	5.3	5.2	5.1	5.1	5.2	5.4		
6 Hr	5.2	5.5	5.2	5.4	5.1	5.3	5.1	5.5		
22 Hr	5.2	5.3	5.3	5.2	4.9	5.1	5.1	5.4		

Table 7. HD in Catalyst Test Solutions under Oxidative Conditions at Time 0, 1, 2, 6 and 22 Hr. – Test 6

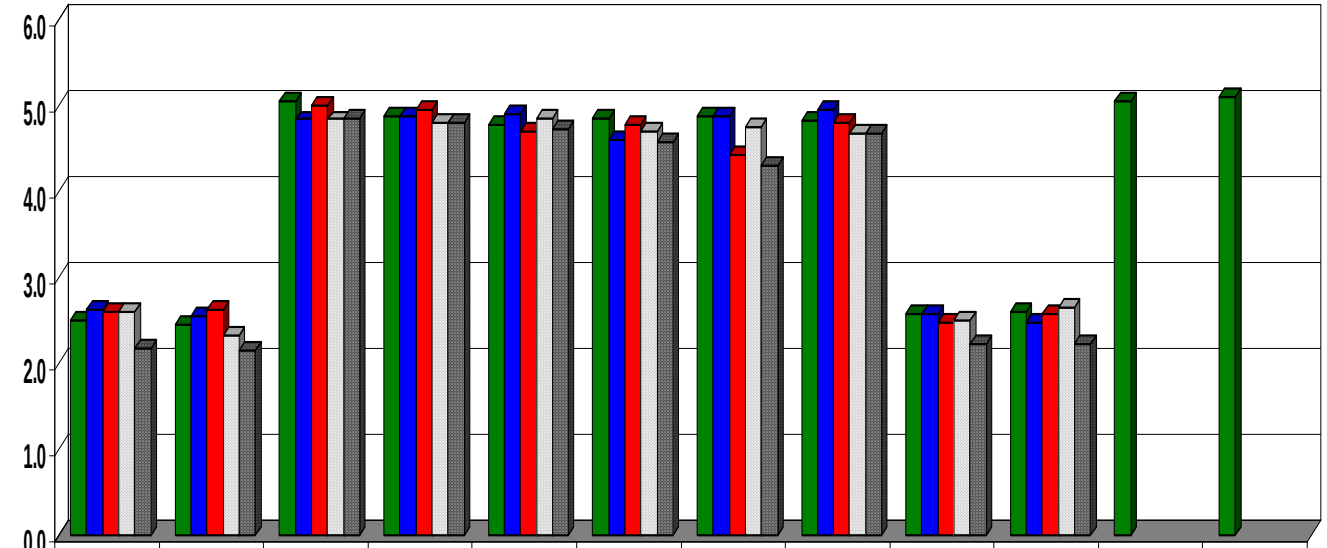
	HD, mg									
Sample Description	0 Hr	%, Theo.[1/]	1 Hr	%, Theo.[1/]	2 Hr	%, Theo.[1/]	6 Hr	%, Theo.[1/]	22 Hr	%, Theo.[1/]
7 Ox HD-1	2.5	98	2.6	103	2.6	102	2.6	103	2.2	86
7 Ox HD-2	2.5	96	2.5	100	2.6	103	2.3	91	2.1	84
8 Ox HD-1	5.1	100	4.8	95	5.0	99	4.8	95	4.9	96
8 Ox HD-2	4.9	96	4.9	96	5.0	98	4.8	95	4.8	94
9 Ox HD-1	4.8	94	4.9	97	4.7	93	4.9	96	4.7	93
9 Ox HD-2	4.9	96	4.6	91	4.8	94	4.7	93	4.6	90
11 Ox HD-1	4.9	96	4.9	96	4.4	87	4.8	94	4.3	85
11 Ox HD-2	4.8	95	5.0	98	4.8	94	4.7	92	4.7	92
Blk6 OX HD-1	2.6	102	2.6	101	2.5	97	2.5	99	2.2	88
Blk6 OX HD-2	2.6	103	2.5	97	2.6	101	2.6	104	2.2	87
Ref 6 OX HD-1 [2/]	5.1	100								
Ref 6 OX HD-2 [2/]	5.1	100								

1/ % Theo. = % Theoretical amount of HD added to MTBE (5.08 mg)

2/ Ref 6 OX HD-1/2 samples were MTBE spiked with HD (5.08 mg) and used as control samples. The samples were also analyzed every 10 samples during a GCMS sequence and no degradation was observed.

3/ Samples 7 OX HD-1 and 7 OX HD-2 consisted of 1 ml TAML solution and 4 ml MTBE spiked with 2.16 mg HD (see Section 2.1). Blk 6 Ox HD-1 and Blk 6 Ox HD-2 were Control samples prepared from 1 ml DI water, 4 ml MTBE and 2.16 mg HD.

Figure 12: Graphical Representation of HD in TDA Catalyst Test Solutions (Test 6)



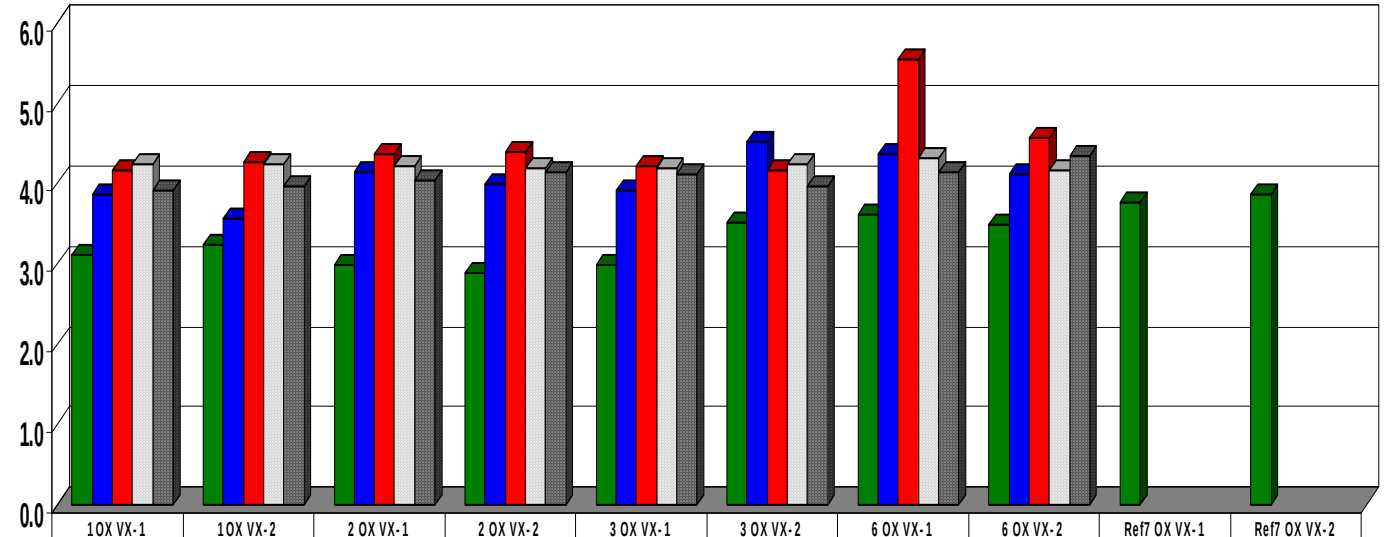
	7 Ox HD-1	7 Ox HD-2	8 Ox HD-1	8 Ox HD-2	9 Ox HD-1	9 Ox HD-2	11 Ox HD-1	11 Ox HD-2	Blk6 OX HD-1	Blk6 OX HD-2	Ref6 Hy GD-1	Ref6 Hy GD-2
0 Hr	2.5	2.5	5.1	4.9	4.8	4.9	4.9	4.8	2.6	2.6	5.1	5.1
1 Hr	2.6	2.5	4.8	4.9	4.9	4.6	4.9	5.0	2.6	2.5		
2 Hr	2.6	2.6	5.0	5.0	4.7	4.8	4.4	4.8	2.5	2.6		
6 Hr	2.6	2.3	4.8	4.8	4.9	4.7	4.8	4.7	2.5	2.6		
22 Hr	2.2	2.1	4.9	4.8	4.7	4.6	4.3	4.7	2.2	2.2		

Table 8. VX in Catalyst Test Solutions under Oxidative Conditions at Time 0, 1, 2, 6 and 22 Hr. – Test 7

	HD, mg									
Sample Description	0 Hr	%, Theo.[1/]	1 Hr	%, Theo.[1/]	2 Hr	%, Theo.[1/]	6 Hr	%, Theo.[1/]	22 Hr	%, Theo.[1/]
1 OX VX-1	3.1	77	3.9	96	4.2	103	4.2	105	3.9	97
1 OX VX-2	3.2	80	3.6	88	4.3	106	4.3	106	4.0	98
2 OX VX-1	3.0	74	4.2	103	4.4	109	4.2	105	4.0	100
2 OX VX-2	2.9	72	4.0	99	4.4	109	4.2	104	4.2	103
3 OX VX-1	3.0	74	3.9	97	4.2	104	4.2	104	4.1	102
3 OX VX-2	3.5	87	4.5	112	4.2	103	4.2	105	4.0	99
6 OX VX-1	3.6	90	4.4	108	5.6	138	4.3	107	4.2	103
6 OX VX-2	3.5	87	4.1	102	4.6	113	4.2	103	4.3	108
Ref 7 OX VX-1 [2/]	3.8	93								
Ref 7 OX VX-2 [2/]	3.9	96								

1/ % Theo. = % Theoretical amount of VX added to MTBE (4.03 mg)
2/ Ref 7 OX VX-1/2 samples were MTBE spiked with VX (4.03 mg) and used as control samples. The samples were also analyzed every 10 samples during a GCMS sequence and no degradation was observed.

Figure 13: Graphical Representation of VX in TDA Catalyst Test Solutions (Test 7)



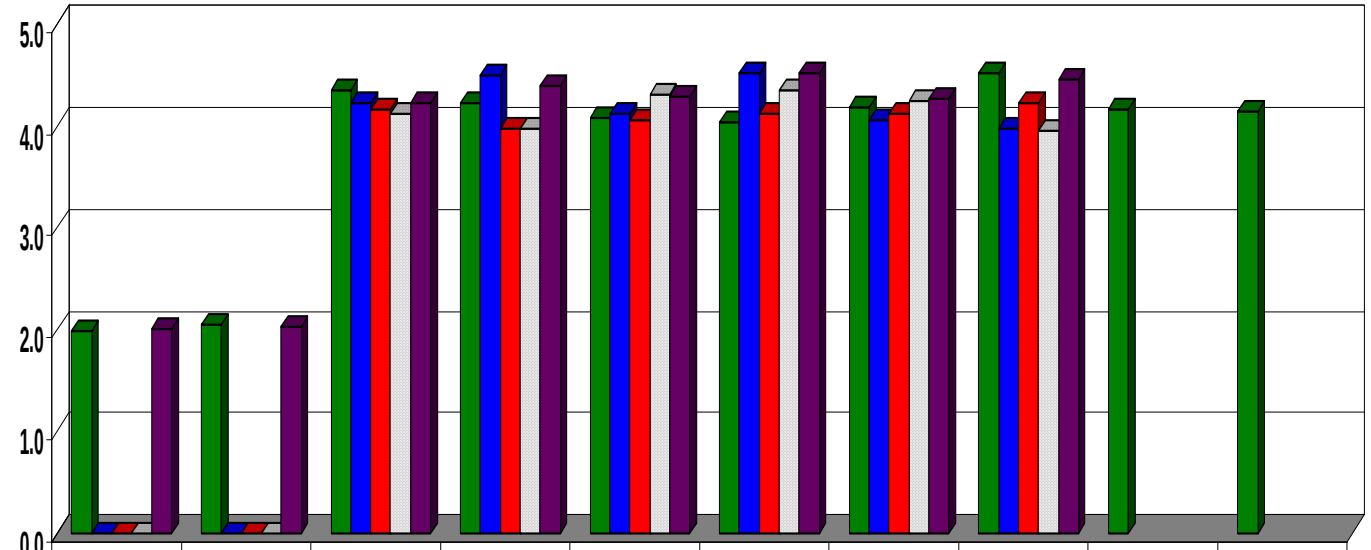
	1 OX VX-1	1 OX VX-2	2 OX VX-1	2 OX VX-2	3 OX VX-1	3 OX VX-2	6 OX VX-1	6 OX VX-2	Ref7 OX VX-1	Ref7 OX VX-2
0 Hr	3.1	3.2	3.0	2.9	3.0	3.5	3.6	3.5	3.8	3.9
1 Hr	3.9	3.6	4.2	4.0	3.9	4.5	4.4	4.1		
2 Hr	4.2	4.3	4.4	4.4	4.2	4.2	5.6	4.6		
6 Hr	4.2	4.3	4.2	4.2	4.2	4.2	4.3	4.2		
22 Hr	3.9	4.0	4.0	4.2	4.1	4.0	4.2	4.3		

Table 9. VX in Catalyst Test Solutions under Oxidative Conditions at Time 0, 1, 2, 6 and 22 Hr. – Test 8

	VX, mg									
Sample Description	0 Hr	%, Theo.[1/]	1 Hr	%, Theo.[1/]	2 Hr	%, Theo.[1/]	6 Hr	%, Theo.[1/]	22 Hr	%, Theo.[1/]
7 OX VX-1	2.0	99	[3/]	[3/]	[3/]	[3/]	[3/]	[3/]	2.0	99
7 OX VX-2	2.1	102	[3/]	[3/]	[3/]	[3/]	[3/]	[3/]	2.0	101
8 OX VX-1	4.4	108	4.2	105	4.2	103	4.1	103	4.2	105
8 OX VX-2	4.2	105	4.5	111	4.0	99	4.0	98	4.4	109
9 OX VX-1	4.1	101	4.1	102	4.1	101	4.3	107	4.3	106
9 OX VX-2	4.0	100	4.5	112	4.1	102	4.4	108	4.5	112
12 OX VX-1	4.2	104	4.1	101	4.1	102	4.2	105	4.3	106
12 OX VX-2	4.5	112	4.0	98	4.2	105	4.0	98	4.5	111
Ref 8 OX VX-1 [2/]	4.2	103								
Ref 8 OX VX-2 [2/]	4.1	103								

1/ % Theo. = % Theoretical amount of VX added to MTBE (4.03 mg)
2/ Ref 8 OX VX-1/2 were MTBE spiked with VX (4.03 mg) and used as control samples. The samples were also analyzed every 10 samples during a GCMS sequence and no degradation was observed.
3/ Samples 7 OX VX-1 and 7 OX VX-2 consisted of 1 ml TAML solution and 5 ml MTBE spiked with 2.02 mg VX (see Section 2.1). These samples had emulsion problems throughout the test, therefore samples were not taken at Time 1, 2, 6. Time 22 Sample was centrifuged and then analyzed.

Figure 14: Graphical Representation of VX in TDA Catalyst Test Solutions (Test 8)



	7 OX VX-1	7 OX VX-2	8 OX VX-1	8 OX VX-2	9 OX VX-1	9 OX VX-2	12 OX VX-1	12 OX VX-2	Ref 8 OX VX-1	Ref 8 OX VX-2
0 Hr	2.0	2.1	4.4	4.2	4.1	4.0	4.2	4.5	4.2	4.1
1 Hr	0.0	0.0	4.2	4.5	4.1	4.5	4.1	4.0		
2 Hr	0.0	0.0	4.2	4.0	4.1	4.1	4.1	4.2		
6 Hr	0.0	0.0	4.1	4.0	4.3	4.4	4.2	4.0		
22 Hr	2.0	2.0	4.2	4.4	4.3	4.5	4.3	4.5		

Table 15. GD Catalyst - Hydrolysis Test Possible Degradation Products Identified by Mass Spectral Library Database – NIST/EPA/NIH Version 2.0 (2002)

Mass Spectral Library Database - NIST/EPA/NIH Version 2.0 (2002)

Retention Time, Min	Name	Most Prevalent Ions	Library Match	Prob.
8.91	N-propyl-butyramide	71,101	786	58.5
9.13	Diisopropyl methanephosphonate	97,123	937	95.9
10.37	Pinacolyl ethylphosphonofluoridate	113,140	899	95.1
11.41	Tributylamine	142,100	898	46.2
11.65	Urea, N,N'-bis(1-methylethyl)-	58,144	831	91.7
12.48	2-Methylcyclohexyl methylphosphonofluoridoate	81,99	901	65.3
12.52	Phosphonofluoridic acid, methyl-, 3-methylcyclohexyl ester	81,99	860	32.2
12.85	O-Isopropyl,O-1,2,2-trimethylpropyl methylphosphonate	123, 97	918	98.9
12.99	O-Isopropyl,O-1,2,2-trimethylpropyl methylphosphonate	123, 97	883	98.1
16.56	Bis(1,2,2-trimethylpropyl) methylphosphonate	123,69	802	91.8
17.03	Acetamide, N,N-dibutyl-	86	744	17.9

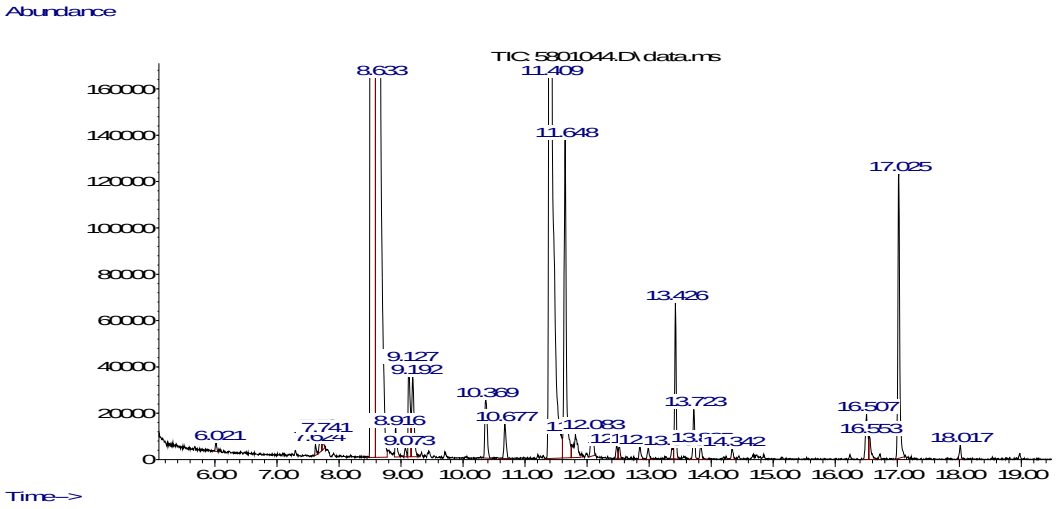


Figure 15: Chromatogram representing 5 Hy GD-1 Time 22

Table 16. Potential GD Catalyst Degradation Products (ug) Identified by GCMS – Hydrolysis Test 3

Sample Description	RT 8.91	RT 9.13	RT 10.37	RT 11.41	RT 11.65	RT 12.48	RT 12.52	RT 12.85	RT 12.99	RT 16.56	RT 17.03
3 Hy GD-1 Time 0	2.5	6.4	6.0	89.4	21.4	6.3	6.2	0.8	0.7	1.5	15.5
3 Hy GD-2 Time 0	2.8	6.3	5.8	89.9	20.9	6.3	6.5	0.7	0.6	1.5	15.0
3 Hy GD-1 Time 1	2.6	6.6	6.1	95.8	22.0	5.8	6.0	0.7	0.7	1.7	16.8
3 Hy GD-2 Time 1	3.0	7.4	5.6	85.1	21.5	5.6	5.5	0.7	0.6	1.7	14.8
3 Hy GD-1 Time 2	2.2	6.8	5.9	121.6	21.9	5.3	4.9	0.7	0.5	1.7	15.8
3 Hy GD-2 Time 2	2.4	6.6	5.7	103.6	20.5	5.0	4.7	0.7	0.6	1.4	15.7
3 Hy GD-1 Time 6	1.5	6.2	5.2	106.0	20.9	2.9	3.0	0.7	0.6	1.5	15.3
3 Hy GD-2 Time 6	2.2	5.7	4.8	94.7	20.1	2.7	2.9	0.7	0.5	1.5	13.7
3 Hy GD-1 Time 22	1.6	4.7	3.9	90.3	20.9	0.7	0.6	0.6	0.5	1.3	14.1
3 Hy GD-2 Time 22	1.5	5.0	4.1	98.9	18.6	0.6	0.6	0.7	0.6	1.4	15.2

Sample Description	RT 8.91	RT 9.13	RT 10.37	RT 11.41	RT 11.65	RT 12.48	RT 12.52	RT 12.85	RT 12.99	RT 16.56	RT 17.03
4 Hy GD-1 Time 0	2.2	7.4	6.1	108.3	20.9	6.3	6.6	0.8	0.6	1.4	15.7
4 Hy GD-2 Time 0	1.7	7.5	6.3	121.3	19.5	6.5	6.6	0.8	0.6	1.6	15.8
4 Hy GD-1 Time 1	2.5	6.3	5.8	119.3	20.0	5.7	5.8	0.7	0.6	1.6	15.8
4 Hy GD-2 Time 1	2.8	7.7	6.7	132.7	20.8	6.5	6.3	0.9	0.7	0.0	18.0
4 Hy GD-1 Time 2	2.2	6.7	5.7	119.6	19.9	5.0	5.1	0.7	0.6	1.4	15.7
4 Hy GD-2 Time 2	2.4	7.2	6.3	122.8	18.9	4.9	5.1	0.8	0.7	1.9	16.1
4 Hy GD-1 Time 6	2.3	6.2	5.3	118.5	19.1	3.0	3.3	0.7	0.6	1.4	15.3
4 Hy GD-2 Time 6	2.0	7.2	5.9	125.7	19.3	3.1	3.3	0.8	0.7	1.7	17.2
4 Hy GD-1 Time 22	1.6	5.0	3.9	119.9	19.8	0.7	0.9	0.6	0.6	1.6	15.4
4 Hy GD-2 Time 22	2.1	6.3	4.9	130.1	18.7	0.8	1.1	0.8	0.8	1.9	17.7
Sample Description	RT 8.91	RT 9.13	RT 10.37	RT 11.41	RT 11.65	RT 12.48	RT 12.52	RT 12.85	RT 12.99	RT 16.56	RT 17.03
5 Hy GD-1 Time 0	2.7	7.7	6.2	83.7	21.0	6.4	6.4	0.8	0.7	1.8	15.1
5 Hy GD-2 Time 0	2.7	6.9	6.3	95.5	22.6	6.6	6.5	0.9	0.7	1.4	16.5
5 Hy GD-1 Time 1	2.6	7.5	6.7	98.9	22.4	6.1	6.0	0.9	0.8	1.9	17.5
5 Hy GD-2 Time 1	2.4	6.8	6.3	95.8	22.5	6.1	5.7	0.9	0.6	1.9	16.7
5 Hy GD-1 Time 2	2.1	8.0	6.6	113.0	21.8	5.2	5.1	0.9	0.7	1.6	17.1
5 Hy GD-2 Time 2	2.0	7.3	6.4	115.7	22.5	5.3	5.2	0.9	0.8	1.7	17.1
5 Hy GD-1 Time 6	2.0	7.2	5.7	106.7	22.0	3.2	3.0	0.9	0.7	1.8	16.9
5 Hy GD-2 Time 6	1.4	4.2	3.8	74.1	15.6	2.1	2.1	0.5	0.0	1.1	10.3
5 Hy GD-1 Time 22	1.8	6.7	4.8	125.0	22.9	0.9	0.7	0.8	0.7	1.6	17.5
5 Hy GD-2 Time 22	1.7	5.8	4.4	125.3	22.3	0.7	0.7	0.8	0.7	1.7	16.5

Sample Description	RT 8.91	RT 9.13	RT 10.37	RT 11.41	RT 11.65	RT 12.48	RT 12.52	RT 12.85	RT 12.99	RT 16.56	RT 17.03
7 Hy GD-1 Time 0	2.7	7.5	6.3	30.2	21.5	6.7	6.6	0.8	0.7	1.4	16.7
7 Hy GD-2 Time 0	2.8	6.1	5.8	29.3	20.9	6.0	5.8	0.7	0.5	1.4	14.7
7 Hy GD-1 Time 1	2.5	7.3	6.4	57.5	22.5	6.6	6.5	0.8	0.7	1.8	17.9
7 Hy GD-2 Time 1	2.5	7.0	6.0	65.8	21.0	6.1	6.1	0.7	0.5	1.5	16.8
7 Hy GD-1 Time 2	2.5	7.2	6.1	61.6	22.0	5.8	5.9	0.8	0.6	1.7	16.4
7 Hy GD-2 Time 2	2.2	6.6	5.6	28.3	21.0	5.6	5.4	0.7	0.6	1.4	15.7
7 Hy GD-1 Time 6	2.0	7.7	6.2	39.4	22.9	5.0	4.8	0.8	0.6	1.5	17.8
7 Hy GD-2 Time 6	2.2	6.5	5.5	46.0	22.6	4.4	4.4	0.7	0.6	1.4	16.1
7 Hy GD-1 Time 22	1.8	6.0	5.4	59.9	22.0	2.8	2.7	0.7	0.6	1.6	15.9
7 Hy GD-2 Time 22	2.0	6.0	5.2	69.4	22.2	2.5	2.6	0.7	0.4	1.4	15.8
Sample Description	RT 8.91	RT 9.13	RT 10.37	RT 11.41	RT 11.65	RT 12.48	RT 12.52	RT 12.85	RT 12.99	RT 16.56	RT 17.03
Blk3 Hy GD-1 Time 0	2.5	7.1	5.6	63.9	21.5	5.9	6.2	0.7	0.6	1.3	14.3
Blk3 Hy VX-2 Time 0	2.4	6.4	6.1	85.1	22.0	6.6	6.4	0.7	0.7	1.6	15.6
Blk3 Hy GD-1 Time 1	2.8	6.5	6.0	85.5	21.7	5.7	5.6	0.7	0.6	1.5	16.0
Blk3 Hy VX-2 Time 1	2.3	6.4	5.7	88.3	20.5	5.6	5.4	0.6	0.6	1.5	15.4
Blk3 Hy GD-1 Time 2	2.5	6.6	5.7	84.1	22.6	5.0	5.0	0.7	0.6	1.3	16.0
Blk3 Hy VX-2 Time 2	2.6	6.9	5.8	119.5	22.1	5.2	5.1	0.8	0.7	0.0	15.8
Blk3 Hy GD-1 Time 6	2.5	6.4	5.3	115.4	22.5	3.2	3.1	0.7	0.6	1.5	15.7
Blk3 Hy VX-2 Time 6	2.1	7.2	5.8	112.1	23.8	3.4	3.4	0.8	0.6	1.8	18.0
Blk3 Hy GD-1 Time 22	1.5	5.1	4.3	96.1	20.6	0.8	0.8	0.7	0.5	1.7	15.2
Blk3 Hy VX-2 Time 22	1.6	4.9	4.1	95.1	21.2	0.8	0.8	0.6	0.5	1.3	15.3
Sample Description	RT 8.91	RT 9.13	RT 10.37	RT 11.41	RT 11.65	RT 12.48	RT 12.52	RT 12.85	RT 12.99	RT 16.56	RT 17.03
H2O Blk3 Hy GD-1 Time 0	2.6	7.9	6.0	101.7	24.9	6.4	6.6	0.8	0.7	1.4	16.3
H2O Blk3 Hy GD-2 Time 0	2.6	6.6	5.6	92.9	20.7	6.0	6.1	0.6	0.5	1.6	14.8
H2O Blk3 Hy GD-1 Time 1	2.3	7.8	5.8	100.3	22.4	6.3	6.4	0.6	0.6	1.6	15.7
H2O Blk3 Hy GD-2 Time 1	2.5	8.1	5.7	99.6	21.3	6.2	6.1	0.7	0.6	1.7	15.7
H2O Blk3 Hy GD-1 Time 2	2.7	7.9	5.7	93.3	23.8	6.0	6.0	0.6	0.6	1.2	14.9
H2O Blk3 Hy GD-2 Time 2	3.0	6.7	5.6	98.4	23.3	6.2	6.4	0.7	0.6	1.5	15.2
H2O Blk3 Hy GD-1 Time 6	2.7	7.8	5.8	36.4	19.2	6.1	6.1	0.7	0.5	1.2	15.4

H2O Blk3 Hy GD-2 Time 6	3.1	6.8	5.7	73.1	20.4	6.2	6.1	0.7	0.6	1.4	15.6
H2O Blk3 Hy GD-1 Time 22	2.6	6.9	6.0	98.1	23.3	6.3	6.3	0.8	0.5	1.7	15.7
H2O Blk3 Hy GD-2 Time 22	2.6	8.2	6.2	104.6	22.8	6.6	6.3	0.7	0.6	1.7	16.4

Table 17. Potential GD Catalyst Degradation Products (ug) Identified by GCMS – Hydrolysis Test 4

Sample Description	RT 8.91	RT 9.13	RT 10.37	RT 11.41	RT 11.65	RT 12.48	RT 12.52	RT 12.85	RT 12.99	RT 16.56	RT 17.03
10 Hy GD-1 Time 0	2.9	6.9	5.2	86.0	24.0	5.7	5.7	0.6	0.5	1.3	12.7
10 Hy GD-2 Time 0	3.2	7.4	5.4	88.2	25.5	6.0	5.8	0.7	0.6	1.3	13.7
10 Hy GD-1 Time 1	2.6	7.2	5.3	80.7	24.8	5.7	5.7	0.6	0.5	1.3	13.1
10 Hy GD-2 Time 1	1.9	6.8	5.3	93.9	24.1	5.4	5.1	0.6	0.5	1.4	13.4
10 Hy GD-1 Time 2	2.3	6.6	5.4	95.3	23.3	4.3	4.4	0.6	0.5	1.3	13.7
10 Hy GD-2 Time 2	2.5	7.2	5.1	92.6	21.6	4.2	4.3	0.6	0.5	1.3	13.9
10 Hy GD-1 Time 6	1.9	6.2	5.0	73.0	35.7	2.5	2.3	0.6	0.5	1.5	14.4
10 Hy GD-2 Time 6	2.0	6.4	5.0	86.9	27.1	2.4	2.4	0.7	0.5	1.4	14.8
10 Hy GD-1 Time 22	1.6	5.4	3.5	83.1	27.4	0.2	0.2	0.5	0.5	1.2	14.0
10 Hy GD-2 Time 22	1.2	5.6	3.6	87.3	25.8	0.0	0.0	0.6	0.5	1.2	14.6

Sample Description	RT 8.91	RT 9.13	RT 10.37	RT 11.41	RT 11.65	RT 12.48	RT 12.52	RT 12.85	RT 12.99	RT 16.56	RT 17.03
12 Hy GD-1 Time 0	2.6	7.2	5.1	90.8	22.0	5.7	5.7	0.7	0.0	1.2	12.3
12 Hy GD-2 Time 0	3.1	7.7	5.3	96.3	23.2	6.0	6.1	0.8	0.6	1.3	13.3
12 Hy GD-1 Time 1	2.5	7.6	5.5	95.2	24.2	5.4	4.9	0.7	0.6	1.2	14.3
12 Hy GD-2 Time 1	2.4	6.4	5.6	102.3	22.1	5.7	5.1	0.6	0.5	1.3	14.2
12 Hy GD-1 Time 2	2.4	6.7	5.4	97.1	21.5	5.0	4.8	0.7	0.5	1.5	14.6
12 Hy GD-2 Time 2	2.6	7.6	5.5	103.4	21.7	4.9	4.9	0.7	0.5	1.3	14.7
12 Hy GD-1 Time 6	2.1	6.9	5.3	95.2	28.9	3.1	3.1	0.7	0.6	1.4	15.5
12 Hy GD-2 Time 6	2.1	6.4	5.1	93.6	28.1	2.8	3.1	0.6	0.6	1.3	14.2
12 Hy GD-1 Time 22	1.4	5.9	3.9	100.1	24.2	0.7	0.7	0.7	0.5	1.3	14.6
12 Hy GD-2 Time 22	1.4	5.7	3.7	97.9	25.2	0.6	0.5	0.5	0.5	1.3	14.8
Sample Description	RT 8.91	RT 9.13	RT 10.37	RT 11.41	RT 11.65	RT 12.48	RT 12.52	RT 12.85	RT 12.99	RT 16.56	RT 17.03
13 Hy GD-1 Time 0	3.4	8.0	5.5	112.9	18.3	5.9	6.4	0.7	0.5	1.3	13.6
13 Hy GD-2 Time 0	3.2	83.9	5.9	119.8	19.2	6.4	6.8	0.7	0.6	1.5	14.9
13 Hy GD-1 Time 1	2.6	7.8	5.8	118.3	18.9	5.7	5.7	0.7	0.6	1.5	14.5
13 Hy GD-2 Time 1	2.6	8.2	5.7	119.9	19.1	5.7	5.9	0.6	0.5	1.2	15.2
13 Hy GD-1 Time 2	2.6	7.6	5.6	119.4	19.0	5.0	5.0	0.7	0.5	1.5	15.1
13 Hy GD-2 Time 2	3.4	9.2	6.2	124.1	20.0	5.0	5.0	0.8	0.6	9.2	17.4
13 Hy GD-1 Time 6	1.9	6.6	5.1	119.2	18.9	3.0	3.2	0.7	0.5	1.6	15.3
13 Hy GD-2 Time 6	1.9	6.8	5.3	121.6	18.7	2.8	3.2	0.7	0.6	1.6	15.0
13 Hy GD-1 Time 22	1.4	5.8	3.7	117.4	19.4	0.6	0.9	0.6	0.5	1.3	14.1
13 Hy GD-2 Time 22	1.3	6.1	3.9	119.0	18.3	0.5	0.8	0.6	0.5	1.4	14.4

Sample Description	RT 8.91	RT 9.13	RT 10.37	RT 11.41	RT 11.65	RT 12.48	RT 12.52	RT 12.85	RT 12.99	RT 16.56	RT 17.03
14 Hy GD-1 Time 0	2.4	7.9	5.9	95.1	21.3	5.9	6.2	0.7	0.5	1.1	14.0
14 Hy GD-2 Time 0	2.1	7.1	5.7	98.7	21.7	6.1	6.1	0.6	0.6	1.5	14.4
14 Hy GD-1 Time 1	2.1	7.3	6.0	111.0	18.6	5.7	5.3	0.7	0.5	1.5	15.5
14 Hy GD-2 Time 1	2.4	8.1	5.9	107.5	21.2	5.7	5.6	0.6	0.6	1.4	14.7
14 Hy GD-1 Time 2	2.5	8.0	5.8	106.4	19.9	4.8	4.6	0.6	0.5	1.5	14.3
14 Hy GD-2 Time 2	1.6	7.5	5.8	104.8	22.9	5.1	4.8	0.6	0.5	1.3	14.8
14 Hy GD-1 Time 6	2.0	6.8	5.4	91.4	25.4	3.0	2.7	0.8	0.5	1.3	14.7
14 Hy GD-2 Time 6	1.8	6.7	5.1	90.6	29.3	3.1	2.8	0.7	0.5	1.3	14.4
14 Hy GD-1 Time 22	1.6	6.6	4.3	114.3	21.3	0.7	0.6	0.6	0.5	1.2	16.1
14 Hy GD-2 Time 22	1.5	5.7	3.7	99.5	23.0	0.6	0.7	0.6	0.5	1.1	13.6
Sample Description	RT 8.91	RT 9.13	RT 10.37	RT 11.41	RT 11.65	RT 12.48	RT 12.52	RT 12.85	RT 12.99	RT 16.56	RT 17.03
Blk4 Hy GD-1 Time 0	3.1	8.0	5.6	92.8	28.6	6.2	6.1	0.7	0.5	1.4	14.0
Blk4 Hy GD-2 Time 0	2.7	7.5	5.1	84.3	28.3	6.0	5.9	0.6	0.5	1.3	12.7
Blk4 Hy GD-1 Time 1	2.5	7.7	5.7	99.6	25.6	5.5	5.5	0.7	0.5	4.7	15.0
Blk4 Hy VX-2 Time 1	2.7	7.5	5.4	99.1	23.9	5.5	5.3	0.6	0.5	1.3	13.2
Blk4 Hy GD-1 Time 2	2.4	7.6	5.6	92.7	27.7	5.0	4.7	0.7	0.6	1.2	14.3
Blk4 Hy VX-2 Time 2	2.4	7.5	5.4	94.9	23.2	4.9	5.0	0.6	0.6	1.4	14.2
Blk4 Hy GD-1 Time 6			Sample Lost								
Blk4 Hy VX-2 Time 6			Sample Lost								
Blk4 Hy GD-1 Time 22	1.4	5.6	3.7	86.1	30.1	0.9	0.7	0.6	0.5	1.1	13.8
Blk4 Hy VX-2 Time 22	1.2	5.4	3.9	89.7	27.1	0.6	0.6	0.6	0.5	1.2	14.3

APPENDIX 1 - SAMPLE SUBMISSION FORM FOR CATALYST TESTING AGAINST CWA'S

TDA

Research

March 28, 2007

Dear Catalyst Researcher:

TDA Research, Inc., under contract to the U.S. Defense Threat Reduction Agency, is soliciting candidate catalysts that may be able to detoxify chemical warfare agents under ambient conditions. DTRA seeks to develop catalytic decontamination capability that would protect against chemical warfare agents without needing to store and transport large volumes of decontaminating liquids. All sample handling and testing will be conducted by the Calspan/University of Buffalo Research Center (CUBRC).

Catalysts are sought that can detoxify one or more of the chemical agents HD, GB, and VX under ambient conditions, presumably using water or oxygen as the ultimate reactant. Catalysts will not be analyzed for any chemical or physical properties other than their ability to detoxify chemical warfare agents and need not be chemically identified beyond providing sufficient data on safe handling and disposal. After testing, catalyst samples will be disposed of and will not be returned, unless special arrangement is made with CUBRC.

Candidate catalysts will be tested if there is a reasonable expectation that they would be shelf stable for prolonged storage (5-10 years) at unregulated temperatures (up to 49 ºC, 120 ºF). Catalysts that are known to produce free radicals are not invited for testing in this program, since free radicals are known to produce complex and potentially dangerous product mixtures.

Catalysts will be eligible for testing whether or not they have been designed to detoxify chemical warfare agents and regardless of the amount of previous testing. Individual researchers may submit multiple catalysts for testing, although budget limitations may dictate how many candidate materials will be tested; *if submitting multiple samples, please indicate a priority order in which they should be tested*. Researchers will be provided with a report documenting the performance of their catalyst samples against chemical warfare agents, including details of the testing protocols and comparisons to other materials tested.

If your organization requires additional assurances to protect intellectual property, please contact Kevin Leous with your organization's requirements:

Kevin W. Leous
Manager, Contracts & Legal
CUBRC
4455 Genesee Street
Buffalo, NY 14225
P: 716-631-6968
F: 716-631-4166
E: leous@cubrc.org

The standard testing protocols are described below for hydrolysis of agents GB (iso-propylmethylphosphonofluoridate) and VX (S-[2-[bis(1-methylethyl)amino]ethyl]-O-ethyl methyl-phosphonothiolate) and for oxidation of agents HD [bischloroethylsulfide] and VX. Blanks and controls are not yet complete, so slight modifications may yet be made to these procedures. If you believe that other tests are appropriate with your materials (e.g. catalytic oxidation of agent GB), please note this on the attached sample submission form. We understand that the conditions in these protocols are not optimal for any particular catalytic system; if the catalyst samples you submit should be tested in a specific solvent system, please note this on the sample submission form and CUBRC will try to accommodate these requests as budget allows.

Standard test protocol for hydrolysis of agents GB and VX:

Use 10 ml buffered aqueous solution (bicarbonate, pH = 8.3). Experiments to be carried out in duplicate in 40 ml glass amber VOA vials. Neat agent (VX or GB) will be added to each vial (equivalent to 12 mg) containing a concentration of catalyst (2.4 mg). The vial will be capped and shaken on a mechanical mixer (at room temperature). Aliquots (1 ml) of the reaction mixture will be removed and transferred to a 7 ml glass vial containing 3 ml chloroform. The vial will be vortexed for 1 min and an aliquot of the $CHCl_3$ will be removed for analysis by GCMS at each time period: T=0, 1, 3, 6, and 20 hrs. The pH of the mixture will be checked with pH paper immediately following extraction. As a control, 10 ml buffered aqueous solution (bicarbonate, pH = 8.3) w/o catalyst will be run along side each set of samples.

Standard test protocol for oxidation of agents HD and VX:

Use 10 ml anhydrous acetonitrile as solvent for the catalyst. Experiments for each catalyst to be carried out in duplicate in 40 ml glass amber VOA vials. Neat agent (VX or HD) will be added to each vial (equivalent to 4 mg) containing a concentration of catalyst (0.8 mg). The vial will be capped and shaken on a mechanical mixer (at room temperature). Aliquots (1 ml) of the reaction mixture will be removed and transferred to 2 ml auto-sampler vial for analysis by GCMS at each time period: T=0, 1, 3, 6, and 20 hrs. As a control, acetonitrile w/o catalyst will be run along side each set of samples.

Thank you for participating in this program.

Best regards,

Bryan Smith, Ph.D.
Senior Chemical Engineer
Phone: 303/940-2331

Sample Submission Form for Catalyst Testing Against Chemical Warfare Agents

Submitting Researcher Name:
Organization:
Mailing address to send report: _____
_____
_____
_____
_____

Sample name:					
Agents to test against (circle all that apply)	VX hydrolysis	GB hydrolysis	HD oxidation	VX oxidation	Other (specify)

General class of sample catalyst materials (e.g. noble metal catalyst supported on silica):
_____
_____
_____

If catalyst is in solution or slurry, please indicate the concentration (mg/ml):_____

Probable mechanism of decontamination reactions: _____Hydrolysis
_____Oxidation
_____Other (please elaborate)
_____
_____
_____
_____

Storage requirements (chemical incompatibilities, temperature limits, etc.):
_____
_____
_____

Safety considerations (known hazards, disposal instructions, etc.):
_____
_____
_____

Preferred reaction solvent system, to be used if budget allows:_____

Please send candidate catalyst samples (at least 5 mg of hydrolysis catalyst or 2 mg of oxidation catalyst per agent selected above) with this completed form to:

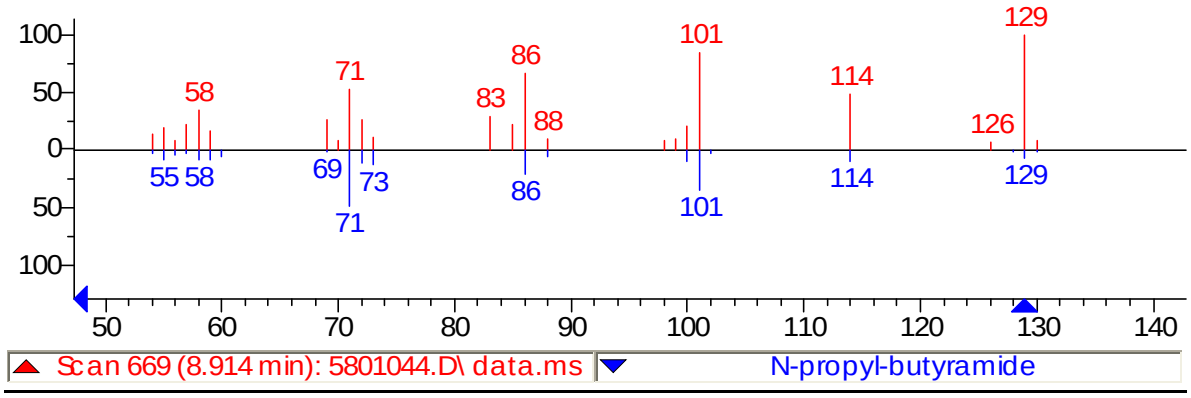
CUBRC
11630 Watson Rd.
Springville, NY 14141
Attn: Meg Stapleton

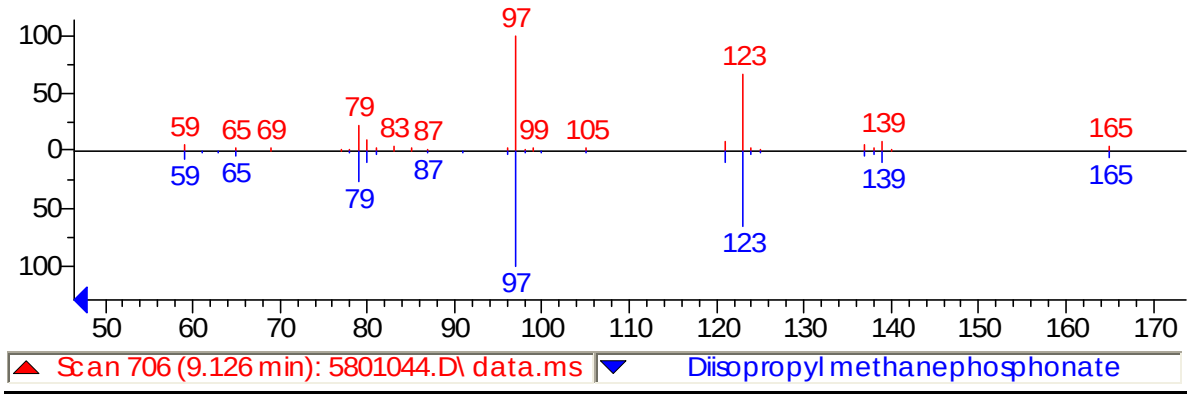
Also, please notify Meg Stapleton by email (stapleton@cubrc.org) that a sample has been sent

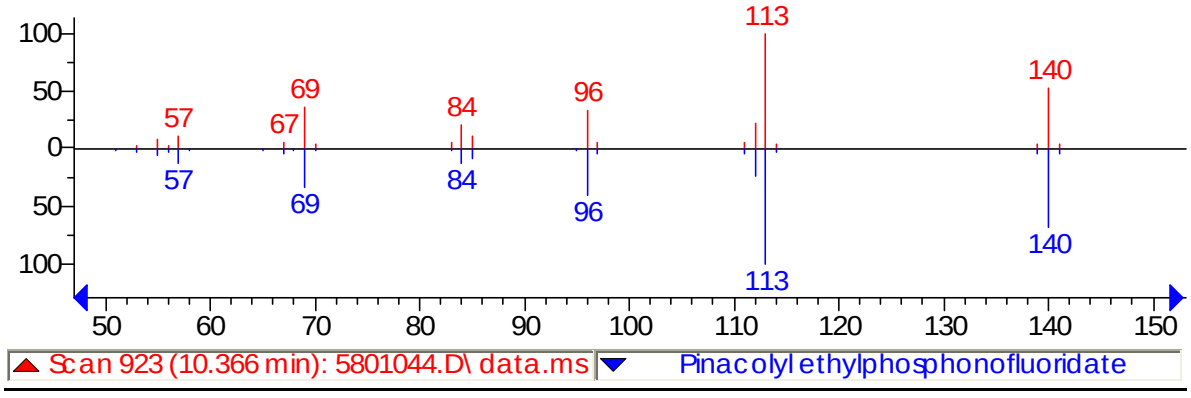
APPENDIX 2 - COMPLETED SAMPLE SUBMISSION FORMS

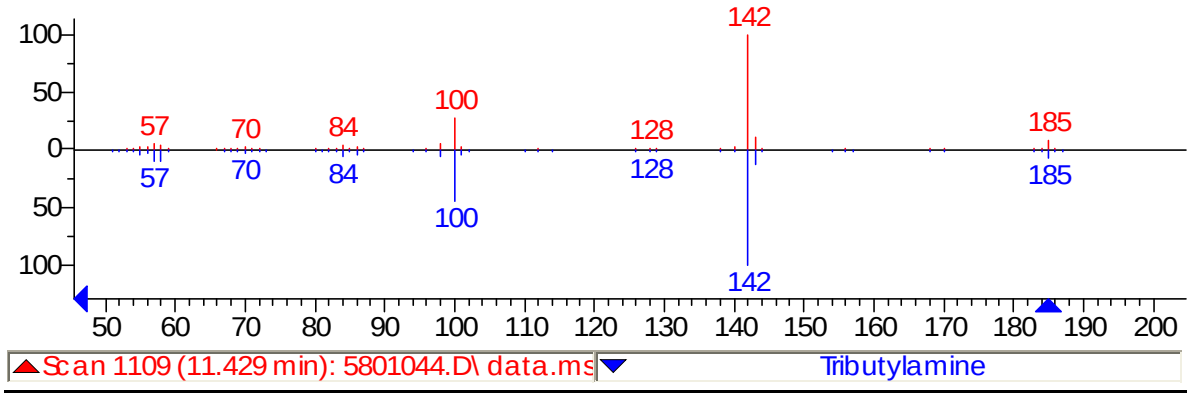
These forms are not included due to the file size, but are available on request from TDA Research, Inc., 12345 West 52nd Avenue, Wheat Ridge, CO 80033. Please contact William Bell at 303-940-2355 or wbell@tda.com

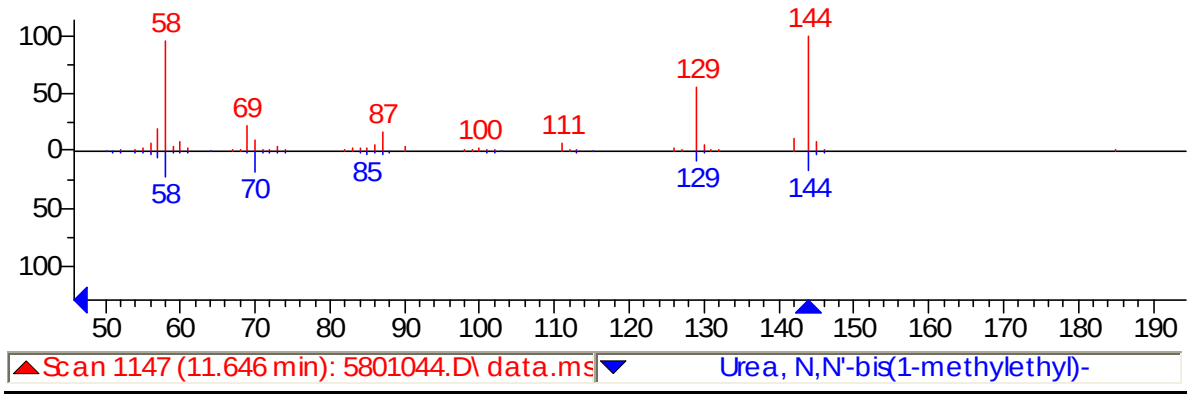
APPENDIX 3 - GD POSSIBLE HYDROLYSIS DEGRADATION PRODUCTS – MASS SPECTRA

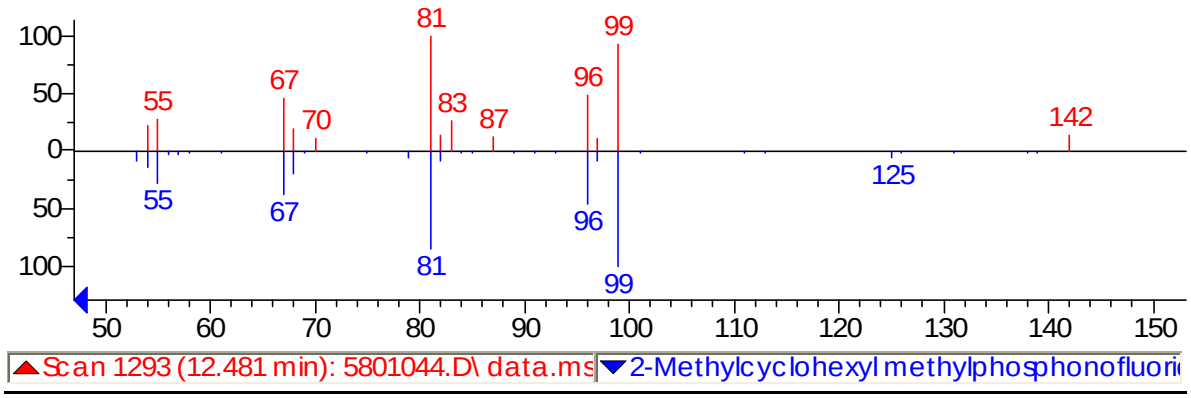

Scan 669 (8.914 min): 5801044.D\ data.ms
N-propyl-butyramide

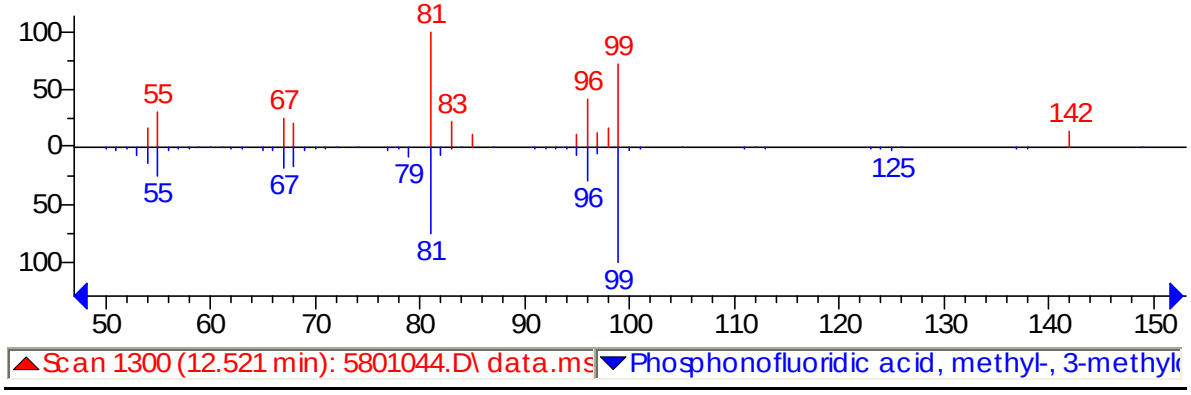

Scan 706 (9.126 min): 5801044.D\ data.ms
Diisopropyl methanephosphonate

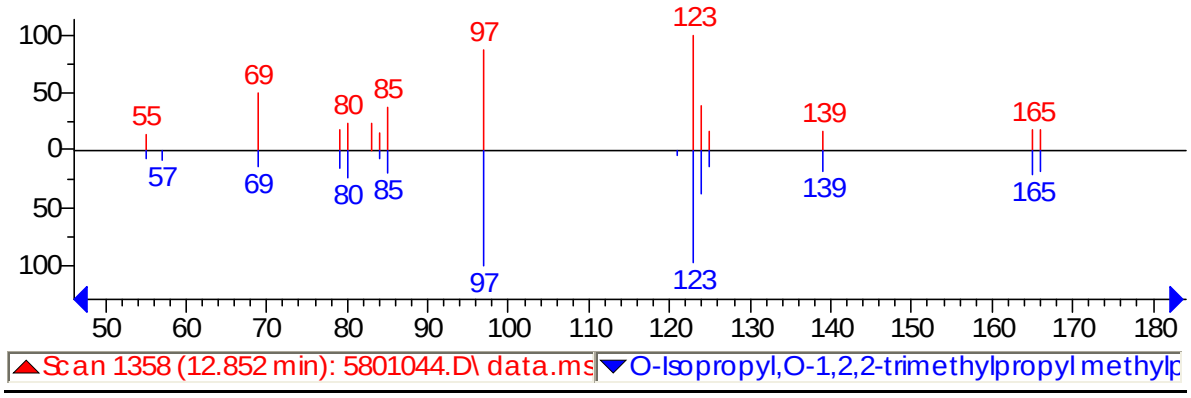

Scan 923 (10.366 min): 5801044.D\ data.ms
Pinacolyl ethylphosphonofluoridate

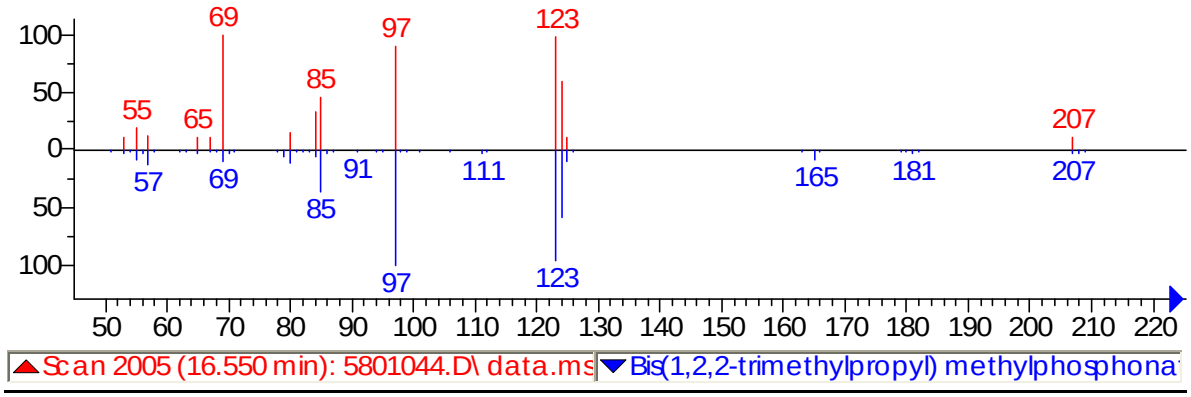

Scan 1109 (11.429 min): 5801044.D\ data.ms
Tributylamine

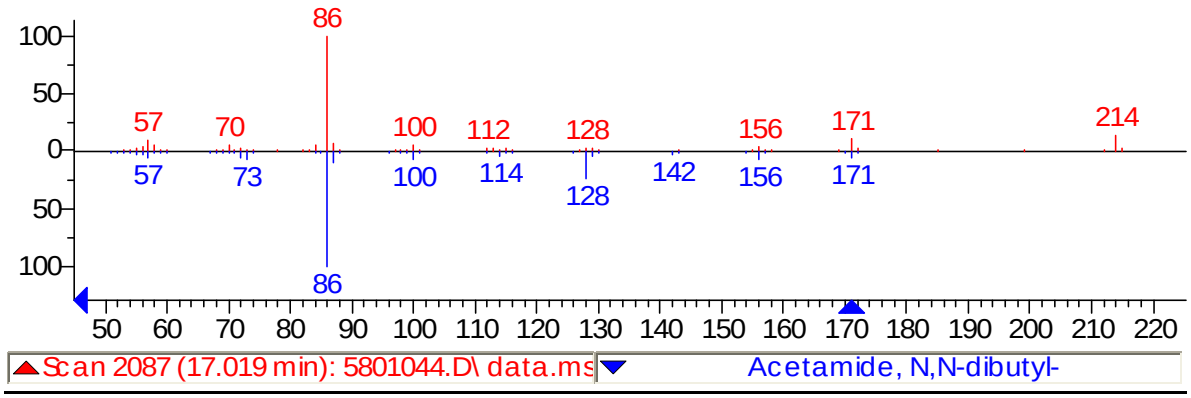

Scan 1147 (11.646 min): 5801044.D\ data.ms
Urea, N,N'-bis(1-methylethyl)-


Scan 1293 (12.481 min): 5801044.D\ data.ms
2-Methylcyclohexyl methylphosphonofluori


Scan 1300 (12.521 min): 5801044.D\ data.ms
Phosphonofluoridic acid, methyl-, 3-methyl


Scan 1358 (12.852 min): 5801044.D\ data.ms
O-Isopropyl,O-1,2,2-trimethylpropyl methylp


Scan 2005 (16.550 min): 5801044.D\ data.ms
Bis(1,2,2-trimethylpropyl) methylphosphona


Scan 2087 (17.019 min): 5801044.D\ data.ms
Acetamide, N,N-dibutyl-

Addendum

November 28, 2006

TDA Research, Inc., under contract from the U.S. Defense Threat Reduction Agency, solicited candidate catalysts to detoxify chemical warfare agents under ambient conditions with no added reagents (only water and air). The above referenced report is the results of the tests of these catalysts, performed by CUBRC, an independent laboratory.

The goal of this study was to identify catalysts that may show some activity against CW agents under ambient conditions, in the presence of only air and water as oxidative species. When soliciting prospective catalysts, TDA received many requests for specific reaction protocols, including solvents. Although these requests were considered in determining experimental protocols, it was impossible to accommodate all of these requests, as the contract for this study specifically mandated a uniform testing procedure for all catalysts

As outlined in the above report, none of the catalysts tested showed any significant activity under these conditions, in either the oxidation or hydrolysis tests. It is important to note, however, that some of these catalysts have shown activity against CW agents and simulants under different conditions (Sorensen and Landry 2005, Chanda et al. 2006), or may be active in different conditions than those tested here (e.g. different temperature, solvent, pH, additional reactants).

One submitted catalyst was subjected to slightly different protocols, as only a small amount of the catalyst was received. Unfortunately, after a modified procedure was determined for this catalyst, a solvent change for the oxidation tests was agreed upon by TDA and CUBRC (the testing facility). This solvent change resulted in a two-phase system for this catalyst (which was dissolved in water). This change may have created an additional challenge for the catalyst. This catalyst has been shown to be effective under different reaction conditions, in the presence of hydrogen peroxide (Chanda 2006).

In conclusion, while this study did not reveal any catalysts that were active under the conditions tested, those conditions were extremely challenging. This study should be understood only as an indication of the catalyst activity under the conditions tested. The study does not imply any activity or lack of activity under other conditions.

Sorensen, Adam C. and Christopher C. Landry (2005). *Catalysis Letters*. **100**, 135-138.

Chanda, Arani, Sushil K. Khetan, Deboshri Banerjee, Anindya Ghosh, and Terrence J. Collins (2006). J. Am. Chem. Soc. 128, 12058 – 12059.